

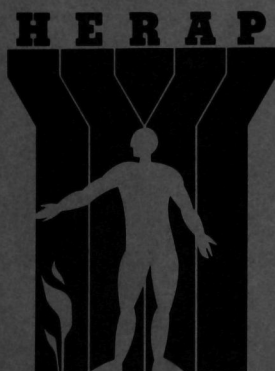
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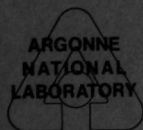
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**HEALTH AND ENVIRONMENTAL EFFECTS
DOCUMENT FOR BATTERIES--1981:
THE ZINC/HALOGEN BATTERIES**



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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Prepared for the Office of Health and Environmental Research
Office of Energy Research**

U. S. DEPARTMENT OF ENERGY

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DOCUMENT FOR BATTERIES--1981:
THE ZINC/HALOGEN BATTERIES

by the

Division of Environmental Impact Studies
and the
Division of Biological and Medical Research

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prepared for

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HEALTH AND ENVIRONMENTAL EFFECTS DOCUMENT FOR
BATTERIES--1981: THE ZINC/HALOGEN BATTERIES

ABSTRACT

This Health and Environmental Effects Document (HEED) is an assessment of the health and ecological effects of the zinc/halogen batteries (zinc/chloride and zinc/bromine) as related to electric and hybrid vehicles and load-leveling applications. As in the past, the storage battery technology has been considered in its totality, and emissions have been estimated for the complete cycle. Emissions have been estimated for the production capability per kWh of battery and for per module of battery. These values are amenable to scaling up as warranted.

Emissions of interest regarding ecological effects are from zinc, titanium, and graphite industries. An analysis of Pb emissions, from the zinc industry, their ecological effects, and movements through the food chains has been attempted.

Health effects as a result of increased levels of Pb, Cd, SO₂ and particulates, and vinyl chloride have been assessed using mathematical models for dose-response relationship. Risks of injury to those employed in battery-related industries are also assessed. Potential health effects of chlorine exposure from accidents involving electric vehicles powered by zinc chloride batteries are evaluated. Health effects of bromine are recognized as potentially important and will be addressed in a subsequent HEED.

1. EXECUTIVE SUMMARY

1. Health and environmental effects due to commercialization of near-term storage batteries (lead/acid, nickel/zinc, and nickel/iron) for electric and hybrid vehicle applications were addressed in the Health and Environmental Effects Document (HEED) for Batteries--1980. Probable health effects resulting from increased levels of lead, arsenic, and cadmium in the environment, and risks of exposure to arsine, stibine, and antimony trioxide released during charging were addressed. The document also contained assessment sections on occupational risk and injury as well as ecological impacts.
2. This Health and Environmental Effects Document (HEED)--1981 is an assessment of the health and ecological effects due to commercialization of the zinc/ halogen electric storage batteries (zinc/chloride and zinc/bromine) as related to electric and hybrid vehicle and load-leveling applications.
3. As in the previous HEED for the near-term batteries, the storage battery technology is considered in its totality, and emissions have been estimated for the complete cycles: (1) mining and milling of the necessary raw materials; (2) manufacture of the batteries and their cases and covers; (3) use of the batteries in electric vehicles and load-leveling substations, including the charge-discharge cycles; and (4) recycling of spent batteries.
4. For the complete cycle, emissions were calculated for the production capability per kWh of battery and per module of the battery--50 kWh/module of zinc/chloride and 20 kWh/module of zinc/bromine battery--on an annual basis. These emission values can be scaled up to any desired production level scenario.

5. For the zinc/chloride batteries, significant emissions estimated for an assumed production scenario of 10^6 modules (50 kWh each) per year are (Table 2.10):

6 MT SO_2 per day

0.06 MT vinyl chloride monomer per day

0.2 MT HCl mist per day

2×10^{-3} MT benzene per day

Major increases in US production for this scenario are indicated for the following materials (Table 2.11):

55% increase in titanium production

25% increase in synthetic graphite production

~500% increase in zinc chloride production

6. For the zinc/bromine batteries, significant emissions estimated for an assumed production scenario of 10^6 modules (20 kWh each) per year are (Table 3.6):

~ 3 MT SO_2 per day

~ 2×10^{-3} MT vinyl chloride monomer per day

~ 5×10^{-4} MT H_2S per day

The major production expansions required for this battery would be for bromine, zinc bromide, and the battery complexing agent plus its production intermediates (Table 3.8).

7. The atmospheric dispersion (Section 4) of the following pollutants produced from industries in the zinc/halogen battery cycle are considered: lead, cadmium, sulfur dioxide, sulfuric acid or sulfates, and vinyl chloride. The industries considered are zinc mining and milling (Pb and Cd), zinc smelting and refining (Pb, Cd, SO_2 , and H_2SO_4) and polyvinyl chloride manufacture (vinyl chloride).

For each industry, two plant sites are analyzed. These were chosen to represent a range of the many parameters of the plant and surrounding area relevant to the effect on public health and environment of the pollutants considered.

For each combination of pollutant and industry site, both the ground-level atmospheric concentrations, and (for Pb only) the deposition rates, are calculated for various receptor positions. The calculations are limited to the near-field region, that is, distances up to 100 km from the plant. They refer to the annual production or capacity of the plant being considered. Appropriate scaling or fractional allocation of a plant to the scenario production of batteries is deferred to later sections.

Calculations are made using an advanced Gaussian dispersion model, the ISC model. Onsite or nearby-site meteorological data are used. The effect of momentum and buoyancy on plume rise is included. The model accounts for gravitational settling and dry deposition by use of gravitational settling velocities and reflection coefficients and can handle particle size distributions as distributions of the settling velocity and reflection coefficient. Chemical transformations are handled by inclusion of an exponential decay factor.

For each pollutant-site combination, near-field average ground-level atmospheric concentration and (for Pb) deposition rates are determined for each of the four seasons. Among the four seasonal isopleth graphs for each pollutant-site combination, two which represent the greatest differences are selected for presentation. These are given as Figures 4.1 through 4.36. It is to be noted that many uncertainties accompany the data.

8. Major emissions of ecological importance are expected to be from zinc, titanium, and graphite industries. The biogeochemistry and ecological effects of As, Cd, Pb, SO₂, and Zn (all related to zinc industry) were described in considerable detail in an earlier report dealing with near-term battery cycles. Available information on titanium and synthetic graphite is summarized in Sections 5.2 and 5.3.

Analysis of lead emissions related to zinc production (Section 5.1) suggests that the additive loading of the environment with lead due to battery-related industry poses risk to aquatic biota in the vicinity of the Missouri site where zinc will be produced for the zinc/halogen batteries in conjunction with mining-milling of lead. Within 100 km of the source, all atmospheric lead deposited due to mining and milling of zinc for the battery industry, if dissolved in rain water, will yield concentrations ranging from 20 to 1200 $\mu\text{g/L}$. The higher levels in this range have been shown to have acute toxic effects on several fresh water species. Bioaccumulation values for lead at such high levels are not available and, therefore, we do not have adequate information to assess the levels of lead that may be found in fish living in the vicinity of this site.

Lead concentration due to battery-related demand for zinc in rainwater runoff for the New Jersey, Pennsylvania, and Texas sites for total lead varies from approximately 20 $\mu\text{g/L}$ near the site to 1 $\mu\text{g/L}$ at 100 km. At such concentrations fish could accumulate approximately 500 $\mu\text{g/kg}$. However, very little of this amount is expected to be accumulated in edible tissues. With this scenario, it is highly likely that the additional burden of lead due to battery industries will result in only a small increase in dietary intake, as compared to the average daily lead intake.

The effects of lead emissions from zinc processing upon terrestrial ecosystems are difficult to predict. Annual simulated accumulation of lead in soils around the sites is expected to exceed Estimated Permissible Concentrations (EPC) at varying distances from the emissions source. This indicates that more rigorous analysis of lead emissions is required before a conclusive assessment of impacts can be made. Simulation of lead deposition indicates that one year's accumulation of lead around smelters is unlikely to have adverse impacts on terrestrial food chains. However, because of our limited understanding of lead biogeochemistry, we cannot confidently anticipate the effects of several years' accumulation of lead due to the battery production scenario.

9. Emissions of interest for health effects analysis are sulfur oxides and particulates, vinyl chloride, lead, cadmium, and chlorine (Section 6.1). Health effects of bromine will be addressed in a subsequent HEED. The effects of these pollutants related to environmental health have been estimated as follows:

The incidence of angiosarcoma of the liver as a result of environmental exposure to vinyl chloride monomer in the vicinity of polyvinyl chloride manufacturing sites is estimated to be insignificant (less than $1/10^{11}$).

At Palmerton, Pennsylvania, a site for projected smelting of zinc sulfide ores, environmental exposure to sulfur oxides and particulates, as a result of production of zinc required for zinc/halogen battery manufacture, is estimated to result in a range of from 5.9 to 31.9 deaths occurring annually in a population of 12,765,000. Reduction of expectation of life, an expression of individual risk, is estimated to range from 0.176 to 0.842 years at this site. Given the natural variation in death rates, it is unlikely that this level of population response would be observed, since such a small variation would be obscured by the changing background values. The impact estimated at the other site analyzed is estimated to be much lower.

The number of people estimated to have a blood lead concentration in excess of 60 $\mu\text{g}/\text{dl}$, as a result of zinc production for battery manufacture, ranges from 0.26 to 1.09, on an annual basis, in a population of 3.27×10^5 at the Missouri site. Estimates of responses at the other sites are smaller.

The number of persons estimated to be at risk annually from renal tubular proteinuria at the end of 30 years of exposure to cadmium at the zinc-producing site in Pennsylvania ranges from 442 to 701 persons in a population of 12,765,000. Estimates of numbers of persons impacted at the other sites range from 0 to 14 persons annually. The risk estimates for cadmium are based on a very conservative definition of tubular proteinuria ($290 \mu\text{g } \beta_2\text{-microglobulin per liter of urine}$).

Estimated chlorine concentrations in the vicinity of accidents involving electric vehicles powered by zinc/chloride batteries and anticipated human responses to these concentrations of chlorine are presented. These data indicate that persons in the vicinity of an accident could be exposed to lethal concentrations of chlorine, with the severity of the exposure depending on the nature of the accident. Concentrations of chlorine listed as potentially lethal to humans after a 30-minute exposure vary over a large range, from 30 ppm to 430 ppm.

10. The effects related to occupational health and safety (Section 6.2) have been estimated as follows:

The excess risk of developing angiosarcoma of the liver following a 35-year exposure to 1 ppm vinyl chloride for 8 hr/day, 5 days/week is approximately 2/100,000,000. Due to small workforce size requirements estimated for making the polyvinyl chloride required for zinc/halogen battery manufacture (260 persons), the number of persons estimated to develop angiosarcoma of the liver from occupational exposure to vinyl chloride as a result of battery manufacture can be considered to be insignificant (0.000,005 persons).

With regard to occupational safety, only persons employed in zinc and titanium primary smelting and refining, and carbon black production, have anticipated injury incidence rates higher than those for the entire private sector. All other industries required for zinc/halogen battery manufacture have occupational injury rates similar to those for the entire private sector. Considering estimates of workforce size along with injury incidence rates, it is estimated that a total of 131 occupational injury cases may occur annually in a work place of 1560 persons during production of materials required for 10^6 zinc/chloride battery modules per year, summing cases for all the industries analysed. The total number of fatalities that may occur annually for all industries analyzed is much smaller (0.1 person per year).

11. It should be stated that there is considerable uncertainty on the technology scene. For FY 1982, the first order of business, therefore, should be to assess the state of the technology before any other assessments are made.

2. EFFLUENTS FROM THE ZINC/CHLORIDE BATTERY CYCLE

2.1 INTRODUCTION

2.1.1 Zinc/Chloride Battery Concept

The zinc/chloride battery is based on an electrochemical cell consisting of a zinc electrode, a chlorine electrode, and an aqueous electrolyte containing 2.0 M zinc chloride.¹ The cell reaction is:



An important auxiliary reaction (in storage of chlorine) is:



where $X \sim 6$; the exact value of X depends on the experimental conditions. The open circuit voltage for the cell is 2.12 V; the zinc/chlorine hydrate system provides a theoretical energy density of 460 Wh/kg (209 Wh/lb).² Reaction (2) requires temperatures below 9.6°C.³

Clearly, the battery concept itself is quite simple, but the utilization of chlorine hydrate (a means of storing chlorine more safely than in gaseous form) leads to considerable complications. The system, as it has evolved at Energy Development Associates (EDA), requires pumping gases and electrolyte through the battery and providing refrigeration to produce the low temperatures needed for chlorine hydrate formation and storage. In order to provide a battery system with an appropriate energy storage capacity, groups of Zn/Cl₂ cells will be packaged as modules to yield a capacity of about 50 kWh per module.

2.1.2 Module Description

The Zn/Cl₂ battery modules proposed to date for use in load-leveling applications and electric vehicles differ in physical appearance but not radically in basic design.^{4,5} Therefore, the salient features of a generic 50-kWh module that would be amenable to either application are considered here.

The major components that comprise the Zn/Cl₂ battery module are the: (a) stack, (b) electrolyte and gas pumps, (c) electrolyte manifold, (d) valving, (e) heat exchangers, (f) H₂/Cl₂ reactor, (g) module case, and (h) control system. An external cooling unit is also necessary, but that system is not considered here to be part of the battery module. A schematic flow chart for such a module⁵ is shown in Figure 2.1.

The stack is composed of bipolar, comb-type submodules containing zinc and chlorine electrodes fabricated of graphite substrates plus associated buses and connectors. The electrolyte is an aqueous solution of ZnCl₂ (2.0 M fully discharged) plus supporting electrolytes circulated by a centrifugal pump magnetically coupled to an external motor; the pump which circulates gases in the module is currently a positive displacement gear pump which is magnetically coupled to an external motor.

The electrolyte manifold provides uniform flow distribution to the cells and is designed to minimize parasitic current losses in the system. The system valving involves normally closed solenoid valves, check valves, and a mechanical pressure-relief valve. There are three heat exchangers: one to remove heat associated with chlorine hydrate formation, another to provide heat for hydrate decomposition on discharge, and a main electrolyte exchanger to remove heat generated during discharge. The heat exchangers are made of titanium tubing.

The hydrogen/chlorine reactor consists of a reactor chamber containing fluorescent lights that photochemically combine hydrogen produced during battery operation with chlorine to form HCl. The module case will be fabricated of plastic fiberglass-reinforced polyester. The microprocessor control

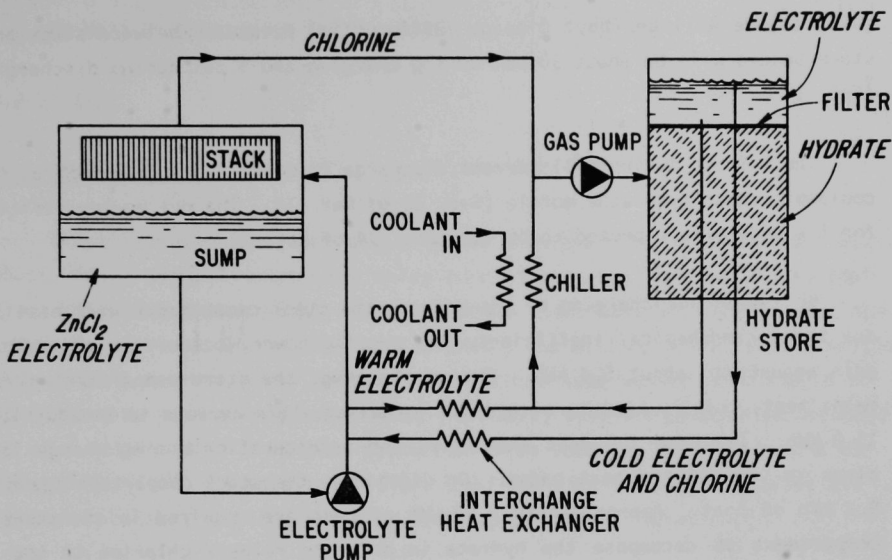


Fig. 2.1. Schematic Flow in Zinc/Chloride Battery Module. From C.H. Chi et al., Proc. 14th Intersociety Energy Conversion Engineering Conf., Boston, 1979.

system modifies stack pressure via a solenoid valve during battery discharge and maintains coolant flow and temperature during charging.

2.1.3 Module Operation

The battery module is essentially a source of direct current electricity with the following characteristics (Sec. 6 of Ref. 6): open-current voltage, 21.2 volts; full-load current, 544 amperes; charging voltage at full-load current, 22.2 volts; discharge voltage at full-load current, 19.6 volts; charge/discharge durations, 7 and 5 hours, respectively.

The module's electrolyte will contain 30 weight percent ZnCl₂ at beginning of charge and 5 weight percent ZnCl₂ at end of charge. On charging, gas pressure in the stack gas space will be about -5 psig; on discharging, stack

gas pressure will be about 0 psig. Differential pressures between stack and store spaces will be about 10 psi during charging and 5 psi during discharging (Sec. 14 of Ref. 1).

The voltage during full-current discharge is quite flat up to ~95% of the coulombic capacity of the module (Sec. 20 of Ref. 1). The net energy efficiency for the module is expected to be 65% (Sec. 14 of Ref. 1).

On seven-hour charging of the module, the stack compartment will heat up due to electrochemical inefficiency and pumping power losses; the net heat gain amounts to about 5.4 kWh. During charging, the store compartment also gains heat, chiefly because of hydrate formation; this amounts to an additional 15.2 kWh. The need for heat exchangers and refrigeration during charge is clear in view of the heat gains. On discharge, the stack compartment gains 9.2 kWh of heat. Approximately 9.59 kWh of heat are required in the store compartment to decompose the hydrate in order to release chlorine to the stack; this is provided chiefly from a heat exchanger.

2.1.4 Input Materials

The major materials used currently in manufacturing a 50-kWh Zn/Cl₂ battery module have been estimated (to one significant figure) to be:⁷

<u>Material</u>	<u>Amount, kg/module</u>
Zinc	50
Chlorine	50
Graphite	70
Titanium	10
Polyvinyl chloride	70
Fiberglass-reinforced polyester	50

It is not unreasonable to expect that some of the quantities will change as the Zn/Cl₂ battery industry develops.

2.2 PRIMARY PRODUCTION OF INPUT MATERIALS

2.2.1 Zinc

Mining and Milling

Zinc-containing ores are widely mined throughout the United States with about 30% of present extraction being concentrated west of the Mississippi River. Lead, and some copper, ores are often associated with zinc; thus, the values for wastes associated with zinc mining and milling given in this section are probably overestimates because they include some wastes that should be attributed to lead mining and milling. In 1974, U.S. ore production amounted to 18.1 million MT;⁸ U.S. zinc production from domestic ores accounted for 315,000 MT (1.7%) of this total (Vol. 1 of Ref. 9). Processing after ore removal involves crushing, grinding, and separation by flotation.

Air Emissions

The chief air-emission sources during mining and milling operations are fugitive dusts resulting from blasting, ore handling, ore crushing, and exposed tailings.¹⁰ Emissions from these operations have been estimated at about 0.2 lb per ton (0.1 kg/MT) of zinc mined (p. 10 of Ref. 10). A more recent study indicates fugitive dust emissions of 0.2 lb/ton zinc from mining and ~ 2 lb/ton ore during crushing (pp. 6-6 to 6-9 of Ref. 11). Assuming current control efficiencies, we can estimate that the total particulate emissions amount to about 0.7 kg/MT zinc. Metal emissions can be estimated on the basis of crude ore compositions for a typical Missouri mine: 4.4% Pb, 2.6% Zn, 0.012% Co, 0.017% Ni, 0.012% Cd, and 0.16% Mn.⁸ Material flows based on these estimates are shown in Table 2.1.

Water Emissions

Mine water drainage is not considered in the wastewater estimates; rather, only water from mill discharges. EPA has estimated that about 3.2 MT wastewater are produced in the milling of one metric ton of ore (Vol 1 of Ref. 12). From this estimate and zinc metal production data, we calculate that about 200 MT

Table 2.1. Estimates of Emissions from the Mining and Milling of Zinc

Emission	Amount, kg/MT Zn	Emission	Amount, kg/MT Zn
AIR		WATER	
Particulates	7×10^{-1}	Wastewater	200,000
Pb	3×10^{-2}	TSS	4
Zn	2×10^{-2}	Zn	1×10^{-1}
Co	8×10^{-5}	Pb	6×10^{-2}
Ni	1×10^{-4}	Hg	2×10^{-4}
Cd	8×10^{-5}	Cd	1×10^{-2}
Mn	1×10^{-3}	Cyanide	2×10^{-2}
		Cu	3×10^{-2}
SOLIDS			
		Mill tailings	40,000

wastewater are produced per metric ton of zinc metal. EPA standards for zinc mill wastes¹³ can be used to calculate the emissions in the wastewater; in reality, standards probably will be more stringent in the time frame of the EV industry. Thus, the estimates given in Table 2.1 are probably conservative.

Solid Wastes

Solid wastes from the mining and milling processes consist chiefly of tailings, as much of the waste rock from mining is used for mine backfilling. Bendersky et al. reported that, in 1974, 12 million MT of zinc mill tailings were produced (dry basis);⁸ from this and the 1974 U.S. production data for zinc we can estimate that about 40 MT of tailings were produced per metric ton of zinc metal. Bendersky et al. indicated the metallic composition of the tailings for a Missouri mine to be 0.093% Pb, 0.018% Cu, 0.083% Zn, 0.0045% Co, 0.0063% Ni, 0.0016% Cd, and 0.18% Mn.⁸ The estimated flow of mill tailings per MT zinc is given in Table 2.1.

Smelting and Refining

Three processes are currently employed in the production of primary zinc: about 45% of domestic zinc is produced by the electrolytic process; 35% is accounted for by the electrothermic process; the remainder is from the vertical retort process. Almost all the new zinc plants use the electrolytic process (p. 204 of Ref. 14). In this process, the ore concentrate, after being roasted, is leached with spent sulfuric acid electrolyte; manganese dioxide is added to oxidize ferrous ions, and the purified solution is plated out on aluminum cathodes in a flowing electrolysis cell, producing a high-purity zinc product.

Air Emissions

To calculate air emissions we have assumed that, when utilization of Zn/Cl₂ batteries is widespread enough to impact the smelting industry, the chief means for primary zinc production will be the electrolytic process. Uncontrolled particulate emissions will, in this case, amount to about 123 kg/MT of zinc metal. Sulfur oxides would amount to 1100 kg/MT of zinc metal (p. 7.7-1 of Ref. 15). Particulate emissions from electrolytic zinc plants have been reported to be nil; particulates lost from the roasting process typically are less than 1% of the feed. Because nearly all the uncontrolled particulate emission would result from roasting, we shall estimate the particulate emission distribution using elemental distributions characteristic of roasting operations (pp. 6-6 to 6-9 of Ref. 11). This approach, coupled with an assumed control efficiency of 99.85% for particulate removal,¹⁶ leads to the values shown in Table 2.2 for particulate emissions. The SO₂ emissions (Table 2.2) were estimated using the 40 CFR standard for zinc roasters¹⁷ (0.065 volume percent SO₂ in discharge gases) and reported off-gas volumes¹⁸ from smelting plants (49 cfm per ton per day of zinc). These values are probably conservative; control technology should be significantly improved in the 1990's, and more stringent standards are likely.

Table 2.2. Particulate and SO₂
Emissions from Primary Zinc
Production

Emission	Amount, kg/MT Zn
As	3×10^{-4}
Cd	1.1×10^{-2}
Pb	1.4×10^{-3}
Sb	3×10^{-4}
Zn	1.7×10^{-1}
SO ₂	42

Water Emissions

The typical electrolytic zinc plant¹⁹ produces about 5.3 m³ of wastewater per metric ton of zinc product, which generates about 9 kg of solids. The roasting of the zinc ores, in addition, produces about 4.7 m³ of acid-blowdown slurry per metric ton of zinc product, containing about 17 kg of solids. Treatment of these wastewaters produces sludges with a combined analysis of: Cd, 802 ppm; Cr, 44 ppm; Cu, 2510 ppm; Hg, 22 ppm; Mn, 8740 ppm; Pb, 15,300 ppm; Se, 66 ppm; and Zn, 220,000 ppm.

Pyrometallurgical zinc manufacturing plants¹⁹ produce (typically) 3.5 m³ of slurries per metric ton of zinc product from gas-cleaning operations, with a solids content of about 94 kg. The acid-blowdown slurries from roasting amount to 13.1 m³, containing 90 kg of solids, per metric ton of zinc product. Retorting operations produce an additional 10 kg of solids per metric ton of zinc product. (These solids are the "blue powder" zinc recovered from the wet scrubber.) Analysis of the combined sludges is typically: Cd, 822 ppm; Cr, 31 ppm; Cu, 540 ppm; Pb, 2920 ppm; Se, 46 ppm; Zn, 206,900 ppm; and Hg, 9 ppm.

To estimate the wastewater emissions from the facilities, we have used the 30-day average effluent limitation guideline²⁰ for primary zinc smelters

utilizing best practicable control technology currently available; these probably yield conservative estimates for facilities that could be operational in the 1990's. Even with these estimates, the quantities emitted in wastewaters are very small (see Table 2.3).

Solid Wastes

Assuming that the electrolytic process for zinc smelting and refining will be the primary source of EV battery zinc, the resulting solid wastes requiring land disposal or storage will be about 26.1 kg of sludge per metric ton of zinc produced.²¹ These sludges will have the composition previously discussed for electrolytic waste sludges (see water emissions). With these values, the amounts of solid hazardous material would be as shown in Table 2.4. Much larger amounts of solid wastes are generated by the smelting process, but the majority of this solid waste is recycled for recovery of metals.

2.2.2 Chlorine

Chlorine is produced by the chlor-alkali industry; in 1979 U.S. production²² of chlorine amounted to 22.22×10^9 lb (1.01×10^7 MT) with an average yearly increase of 2.6% over the years 1969-1979. About two-thirds of U.S. chlor-alkali production results from brine electrolysis in diaphragm cells; since it is expected that nearly all future U.S. production will be by this process,²³ we have made our emission estimates based on the diaphragm-cell process. Emission standards for the chlor-alkali industry are usually formulated relative to chlorine production.

Air Emissions

The major source of air emissions in chlorine production is from chlorine blow gas produced during chlorine liquefaction. Normal plant operation results in an emission factor of 5×10^{-3} kg chlorine per metric ton of chlorine liquified.²³ In addition, small amounts of carbon monoxide may be emitted with the blow gas (about 0.4 volume percent of the exhaust gas);²³ this corresponds to about 8×10^{-2} kg CO per metric ton of chlorine liquified, assuming no CO absorption equipment in the control system. This is probably a very

Table 2.3. Wastewater Emissions from Primary Zinc Production

Emission	Amount, kg/MT Zn
TSS	2.1×10^{-1}
As	8×10^{-4}
Cd	4×10^{-3}
Pb† ¹	4×10^{-3}
Se	4×10^{-2}
Zn	4×10^{-2}

Source: E. Isenberg et al., Report PB 278 800, March 1977.

†¹ Not explicitly listed in 40 CFR 421.83, but assumed to be the same value as CD.

Table 2.4. Solid Emissions from Primary Zinc Production

Emission	Amount, kg/MT Zn
Total sludge	26.1
Cd	5.6×10^{-2}
Cr	1.1×10^{-3}
Cu	6.6×10^{-2}
Hg	5.7×10^{-4}
Mn	2.3×10^{-2}
Pb	4.0×10^{-1}
Se	1.7×10^{-3}
Zn	5.7

conservative estimate of the CO releases and more stringent regulations in the future could result in significant reduction of this already small air emission. Table 2.5 summarizes the air emission estimates.

Water Emissions

We shall assume that for new sources, standards of performance in 40 CFR 415.65 will be implemented in plants producing chlorine for the Zn/Cl₂ battery; the 30-day average emission values are: 0.32 kg of suspended solids/MT of product, 4×10^{-5} kg of lead/MT of product, and a pH within the range 6.0 to 9.0. The emissions involved for the chlorine content of a Zn/Cl₂ module are given in Table 2.5. The quantities of pollutants emitted in the liquid waste streams should be very small.

Table 2.5. Estimated Emissions from Chlorine Production

Emission	Amount, kg/MT Cl ₂
AIR	
Chlorine	5×10^{-3}
Carbon monoxide	8×10^{-2}
WATER	
TSS	3.2×10^{-1}
Pb	4×10^{-5}
SOLIDS† ¹	
Total solids	~ 4
Pb solids	2×10^{-1}
Chlorinated hydrocarbons	4×10^{-1}

†¹ Dry basis (sludge is 30% solids).

Solid Wastes

In 1974, about 6 kg of dry solid wastes destined for land disposal were produced by the chlor-alkali industry per metric ton of chlorine;²³ this amount includes asbestos and mercury, which should not be emitted from plants producing chlorine for Zn/Cl₂ batteries. Based on data for a typical chlor-alkali plant,²⁴ we can estimate that the total dry solid wastes would amount to about 4 kg/MT chlorine. Solid emission estimates based on these data are shown in Table 2.5; these values represent current technology and will probably be conservative in relationship to plants operating in the 1990s.

2.2.3 Hydrochloric Acid

Hydrochloric acid is necessary for the production of zinc chloride. Most of the HCl is produced as a by-product of other processes, chiefly the chlorination of organic compounds; thus, the emissions associated with its production

should be charged to the more valuable organic compounds. However, we shall consider that the acid mist generated in the by-product manufacture of HCl is applicable in our considerations; this amounts to 1.5 kg HCl per MT of by-product hydrochloric acid,²⁵ or about 0.08 kg of hydrochloric acid mist per 50-kWh battery module.

2.2.4 Zinc Chloride

Zinc chloride is prepared chiefly by reaction of zinc or zinc dross with hydrochloric acid. The only wastes from the process are product purification solids (from evaporation and filtration), which are then reprocessed.²⁶ Therefore, for our considerations, the small effluent release from this latter process will be disregarded. The production of a metric ton of $ZnCl_2$ requires about 50 kg chlorine gas, 480 kg zinc, and 530 kg HCl.

2.2.5 Titanium

Mining and Milling

Essentially all the titanium produced in the United States derives from rutile,²⁷ a nearly pure TiO_2 . Since virtually all this rutile ore is imported, no emissions will be charged against rutile mining and milling in this report. Ilmenite, which is mined in the U.S., is not an economical ore for reduction to metallic titanium.²⁸

Chlorination and Purification

The titanium ore is converted to $TiCl_4$ by chlorination; about 2.5 MT of chlorine are used per metric ton of rutile²⁸ (much of the chlorine is recycled). Effluent gases from the $TiCl_4$ manufacturing process have been reported as 38 kg Cl_2 , 13 kg HCl, and 12 kg per ton of $TiCl_4$ produced.²⁸ Sludges from the chlorination process produce the only significant solid waste, amounting to about 330 kg per MT of titanium sponge.²⁷ The water soluble content (ppm) of these sludges is: 25,780 V; 11,630 Cr; 34,770 Zr; 104,400 Ti; and 187,000 Cl.²⁷ Currently these sludges (23% solids) are disposed of by landfill burial or lagoon storage.¹⁹ Normal operation should produce no waterborne waste.²⁹

Estimated emissions for the chlorination and purification portion of the titanium production process can be obtained from these data and are presented in Table 2.6. Gaseous emission control efficiencies were estimated at 99.9% for these calculations.

Table 2.6. Estimated Emissions from Chlorination and Purification of Titanium Ore

Emission	Amount, kg/MT Ti
AIR	
Chlorine	0.3
HCl	0.1
TiCl ₄	0.1
SOLIDS	
Sludge† ¹	360
V	9.3
Cr	4.2
Zr	13
Ti	38
Cl	67

†¹ Sludge is about 23% solids.

Reduction and Fabrication

The reduction process for preparation of metal from TiCl₄ takes place in a closed system in which magnesium is used as the reductant (Kroll process). What effluents do result from this process have already been included in the chlorination and purification step²⁷. Magnesium chloride produced by the reduction is processed to recover the elements; thus, the production of 1 kg of sponge metal requires only about 0.2 kg Mg and 1 kg of chlorine.²⁸ These values convert to 0.003 MT Mg and 0.01 MT chlorine per 50-kWh battery module.

The fabrication step involves about a 9% loss of Ti sponge;²⁸ we shall assume that about 10% of these losses are associated with grinding and surface finishing operations on sheet and finished tubing (leading to particulate emissions). Assuming an efficiency of 99.5% for the particulate emission control equipment, we can estimate release of about 0.04 kg of Ti-containing particulate per MT of finished titanium tubing.

2.2.6 Graphite

The starting materials for graphite production are petroleum coke, made from refining distillation residue, and coal-tar pitch.³⁰ Production steps involve crushing and sizing the coke, mixing in the pitch (which acts as a binder), forming the mixture into a desired shape, baking to pyrolyze the pitch, and finally, graphitization by heating to $\sim 3000^{\circ}\text{C}$ in an electric furnace.³¹ Although the graphitization furnace in use today was invented in 1895, there are little data in the literature dealing with emissions from graphite production. Graphite is classified as a nuisance dust, although it should be controlled to levels of 10 mg/m^3 .³²

A recent study indicates that significant amounts of polynuclear aromatics (including benzo(α)pyrene) can be found on analysis of air particulate samples collected during graphite production.³³ In that study the highest emissions were found to occur during grinding of the pitch-modified cokes. That carcinogenic materials can be emitted from graphite production has also been observed for industrial-scale operations in the Soviet Union.³⁴

Clearly, emissions from the graphite processing must be kept at minimal levels. Grinding operations can be performed in automatic closed-system facilities utilizing cyclones and bag filters to separate particulates; the air from such a system is recycled.³⁵ Thus, the levels of emissions from graphite production can be reduced to essentially nil. We shall assume this to be the case in the time-frame of large-scale application of the Zn/Cl_2 battery. Recycling and incineration will dispose of any solid wastes from the processing.

Emissions from petroleum coking and pitch production will not be considered here since the amounts used for graphite manufacture are minute compared to total U.S. production.

2.2.7 Polyvinyl Chloride

Polyvinyl chloride (PVC) is manufactured in the United States by a number of processes, the most common of which is the suspension process.³⁶ This process involves suspension of liquid vinyl chloride in a continuous water phase under pressure. A free radical catalyst initiates the polymerization reaction; after polymerization is complete, the vinyl chloride monomer is stripped from the polymer slurry. The slurry is then centrifuged and dried to yield raw PVC resin, which is then compounded and manufactured.

Vinyl Chloride Monomer Production

The vinyl chloride monomer ($\text{CH}_2\text{ClCH}_2\text{Cl}$) is produced chiefly by either chlorination or oxychlorination of ethylene.³⁷ Ethylene production in the United States in 1979 was 29.2 million pounds; the vinyl chloride produced amounted to 7.5 million pounds.³⁸ Emissions from ethylene production will not be considered here since it is a by-product of the petroleum industry and would be assessed there.

Estimation of emissions from vinyl chloride monomer (VCM) production was based on an assumed emission reduction³⁹ of about 94% (through the use of improved environmental control technology) (Table 3.5 of Ref. 39). The resulting emission values are: in air, 0.3 kg per MT VCM produced; in process water, 4×10^{-4} kg per MT VCM produced. There would be other emissions such as HCl and chlorine in air and caustic soda in process water,³⁷ but emission controls should readily reduce them to virtually zero.

From a materials-use standpoint, production of VCM utilizes about 0.3 MT of chlorine per MT of monomer produced.

Polyvinyl Chloride (PVC) Production

The suspension process for PVC production will be assumed to have a 95% emission reduction capability.³⁹ Utilizing data for PVC process emissions (Table 3.6 of Ref. 39), we can estimate air emissions of VCM as 2 kg per MT of PVC and process water emissions of 0.01 kg VCM per MT of PVC. A more recent study²⁵ has estimated achievement of better emission controls (99% or more) with reduction of these emissions to about 0.04 kg/MT of PVC; particulate (PVC) in the air emissions would amount to 0.2 kg/MT of PVC. Solids wastes can be estimated³⁶ at about 10 kg PVC per MT of product; however, rather than using landfill disposal of the solids in the future, there is likely to be greater recycle of the PVC or possibly combustion to recover energy. Therefore, we shall not consider the PVC solid wastes in this case.

From a material balance standpoint, we shall assume that 1.05 MT VCM is necessary to produce a metric ton of PVC.³⁶ Therefore, for production of a metric ton of PVC, no significantly greater amount of chlorine will have been used than for production of a metric ton of VCM.

2.2.8 Fiberglass-Reinforced Polyester

Fiberglass-reinforced plastics are widely used for chemical process equipment because of their toughness and corrosion resistance. In connection with the ZnCl_2 battery module we shall consider a fiberglass (25%) reinforced polyester (FRP) material. The case can be fabricated from this material by a number of means, including injection-molding, vacuum molding, compression molding, and hand lay-up techniques (p. 33-10 of Ref. 1). Emissions from any of these fabrication methods should be minimal compared to those from producing the case materials themselves.

Polyester Resin Production

Most of the thermosetting reinforced plastics are made from polyester resins (p. 141 of Ref. 40). Polyester resin production results from polymerization of a dibasic acid or anhydride with a dihydric alcohol followed by cross-linking using a reactive monomer such as styrene. Thus, the production

of polyester resin can involve many organic compounds as feed materials; typical ones are phthalic anhydride, maleic anhydride, glycols (propylene, ethylene, diethylene) and usually styrene.⁴¹

Estimates of air emissions (as "oil mists") from polyester resin manufacture indicate a value of about 0.2 kg per MT resin.²⁵ The composition of the oil mist would depend on the formulation of the resin. Assuming that the mists arise in the polymerization step and that the input to the reaction consists of approximately equimolar amounts of phthalic anhydride, maleic anhydride, propylene glycol, and ethylene glycol (p. 116 of Ref. 41), we can estimate the mists could contain (per MT resin): phthalic anhydride, 0.06 kg; maleic anhydride, 0.04 kg; propylene glycol, 0.03 kg; ethylene glycol, 0.03 kg; and water 0.04 kg. The estimated values for the anhydrides are probably too high since the anhydrides would be solids and probably not as easily dispersed as the liquid glycols. Thus, the emissions listed above are probably quite conservative.

Liquid wastes from the process are subjected to recycle, scrubbing, and incineration and should be minimal in terms of organic pollutant content.⁴² Solid waste also would be recycled or burned for waste heat recovery. Therefore, we shall not consider solid or liquid effluents from the process.

Maleic anhydride and phthalic anhydride, which are used in production of the polyester, are synthesized from benzene or its derivatives and, hence, would be subjected to stringent emission controls. Estimates of controlled air emissions for these processes are available in the literature; however, they seem much too large* for phthalic anhydride in the light of available pollution control technology.²⁵ Washing of the waste gases in scrubbers results in at least 98-99% removal of residual organics, and blowdown of this material to an incinerator produces nonpolluting products.⁴² For our purposes, the efficiency of emission control technology will be assumed to be 99.9%, leading to the following estimates of air emissions per metric ton of polyester

*Estimated emissions: maleic anhydride manufacture, 0.09 kg hydrocarbon (chiefly benzene) and 0.7 kg CO per MT product; phthalic anhydride, 2.5 kg hydrocarbon and 0.1 kg CO per MT product.²⁵

resin; benzene, 0.016 kg; xylene, 0.019 kg; and CO, 0.16 kg. Liquid and solid wastes are assumed to be zero.

Data on emissions from production of propylene glycol are not readily available in the literature; our estimates are based on emissions proposed²⁵ for ethylene oxide production by means of air oxidation. The manufacturing processes are not too dissimilar; however, our estimate of amount of emissions, 0.02 kg of hydrocarbons (chiefly propylene, ethane, and methane) per metric ton polyester resin, should be regarded as order of magnitude values only. This estimate is based upon a 99.9% efficiency for the emission control systems; liquid and solid wastes are assumed to be zero.

The amounts of styrene and ethylene glycol that would be utilized in making a million ZnCl_2 modules would be miniscule compared with the amounts produced for other purposes; therefore, the emissions from the manufacture of styrene and ethylene glycol have been ignored for this report.

Fiberglass Production

Textile fiberglass is typically manufactured by melting and forming fibers from glass marbles. The fibers are collected on spools as continuous filaments or as mats on a flat surface. In 1979 production amounted to 459,000 MT. The emissions from this process are particulates, sulfur dioxide, carbon monoxide, nitrogen oxides, and fluorides.⁴³ The amount of these emissions per metric ton of fiberglass have been estimated as:¹⁸ particulates, 0.76 kg; SO_2 , 0.02 kg; NO_x , 1.4 kg; CO, 0.78 kg; and fluorides, 0.01 kg. Liquid and solid effluents are assumed to be zero.

Combined Emissions

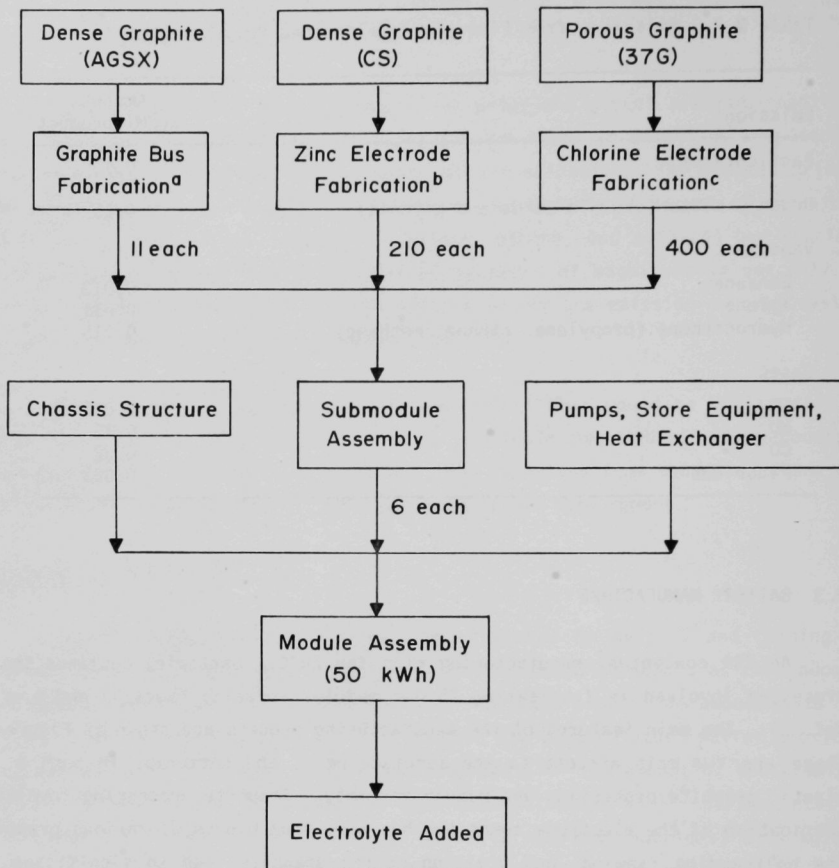
The estimated combined emissions for FRP are given in Table 2.7. These estimates are based on the assumptions that there will be 25% fiberglass in the resin and no significant releases from fabrication of the battery module cases.

Table 2.7. Emissions from Fiberglass-Reinforced Polyester Manufacture

Emission	Amount, kg/MT product
Particulates	0.19
Organic mists (organic acids and glycols)	0.15
Vapors	
Benzene	0.012
Xylene	0.014
Hydrocarbons (propylene, ethane, methane)	0.015
Gases	
SO ₂	0.005
NO	0.35
CO ^x	0.32
Fluorides	0.003

2.3 BATTERY MANUFACTURE

An EDA conceptual manufacturing plan for Zn/Cl₂ batteries outlines the processes involved in fabricating 25,000 modules annually (Secs. 7 and 8 of Ref. 1). The main features of the manufacturing process are shown in Figure 2.2. There are two main aspects to the manufacture of the batteries in such a plant: graphite processing and module assembly. Graphite processing involves fabrication of the electrode combs and bus bars from blocks of various graphite. The beltsanding, sawing, and drilling of the graphite lead to significant material loss, including airborne dusts. Because of these losses, graphite processing is the most expensive step in this battery-manufacturing plan. Module assembly involves combining previously fabricated or purchased component hardware items such as gas pumps, heat exchangers, electrical connectors, battery case, etc., with the graphite electrode submodules to produce a completed module. The final process step would be filling the battery with electrolyte and testing; shipping of the battery to its user would be without the electrolyte in place.



^a Fabrication losses ~ 28%

^b Fabrication losses ~ 49%

^c Fabrication losses ~ 44%

Fig. 2.2. Diagram of the Zinc/Chloride Battery Manufacturing Process (25,000 modules per year). From Energy Development Associates, "Development of the Zinc-Chloride Battery for Utility Applications." EPRI EM-1051, April 1979.

Based on the cost figures in Ref. 1, one can estimate that about 41% of the total graphite used would be lost during fabrication; however, it seems likely that for a mature technology this value should be reduced. Because of the absence of appropriate guidance in the literature for a mature industry, we shall assume a 25% loss in graphite processing at the time of commercialization of the Zn/Cl_2 battery. This leads to an estimated processing loss of about 23 kg of graphite per module. If 0.5% of this graphite becomes airborne as dust and the dust control system employed has state-of-the-art efficiency, the release of graphite particulate to the air would be about 0.001 kg per 50-kWh module. The graphite solids collected by control equipment would probably either be recycled for recovery or incinerated, leading to minimal solid waste for disposal.

The module assembly process should lead to virtually no releases because it involves no fabrication. Preparation of the electrolyte and loading it into the modules could be expected to have little spillage, certainly less than one percent, with liquid releases of less than 0.5 kg of ZnCl_2 per module. This material can be expected to end up in the waste treatment facility of the plant, with about 0.2 kg of zinc going into the sludge product of the plant and most of the chloride released as liquid effluent.

2.4 NORMAL OPERATION

The battery module is designed so that under normal operating conditions no emissions occur except for small releases of CO_2 at the end of the module discharge period.⁴

2.5 RECYCLING

The commercial lifetime of the Zn/Cl_2 battery module will exceed ten years,¹ and it seems unlikely that a specialized "scrapper" industry will develop for recovery of these batteries alone; however, recycle of such batteries would probably involve metallurgical recovery of the titanium-based hardware, reworking of pumps, probably reconditioning of the electrolyte, and discarding of the graphite electrodes. It seems reasonable to assume that in the timeframe of commercialization of the Zn/Cl_2 battery module, emission

standards will be stringent and only minimal amounts of ZnCl_2 will be disposed of in landfills. The reject graphite probably will be disposed of through incineration. Thus, the recycle process should result in the release of few emissions other than CO_2 from graphite combustion and chloride released in water within environmentally prescribed limits.

2.6 TOTAL CYCLE

The emissions estimated for the total Zn/Cl_2 battery cycle are summarized in Table 2.8 for a 50-kWh module. These values should be considered as preliminary estimates only because the Zn/Cl_2 battery design and manufacturing processes are still in the development stage.

2.7 COMMERCIALIZATION

2.7.1 Load-Leveling Applications

Concepts have been presented for the design of a 100-MWh battery plant for load-leveling applications (Sec. 6 of Ref. 4); these plants are based on a battery module with a slightly greater capacity than 50 kWh. We shall assume, however, that the same number of 50-kWh modules would be used in such a plant. Thus, we consider here the emissions resulting from the use of 2000 battery modules per plant. We shall not consider here the environmental impact of refrigeration units, control units, and other items peculiar to the load-leveling application of these batteries.

The large-scale load-leveling plant (100 MWh) under current design contains 32 racks, each with 60 individual Zn/Cl_2 battery modules (Sec. 6 of Ref. 6). The racks are 18 ft high and the whole site occupies a rectangle about 180 by 138 ft. Refrigeration and coolant equipment are to be located in the center aisle of the facility.

The emissions estimated to result from the use of Zn/Cl_2 batteries in such 100-MWh plants are given in Table 2.9. It has been estimated by EPA that about 250 such plants installed annually could meet the load-leveling needs of

Table 2.8. Estimated Emissions from the Zinc/Chloride Battery Cycle

Emission	Amount, kg/50-kWh module	Emission	Amount, kg/50-kWh module
AIR		WATER	
Particulates	5×10^{-2}	Zn	4×10^{-1}
Pb	1×10^{-3}	Pb	3×10^{-3}
Zn	9×10^{-3}	Hg	6×10^{-6}
Co	4×10^{-6}	Cd	7×10^{-4}
Ni	5×10^{-6}	Cyanide	9×10^{-4}
Cd	5×10^{-4}	Cu	1×10^{-3}
Mn	5×10^{-5}	As	4×10^{-5}
As	1×10^{-5}	Se	2×10^{-4}
Sb	6×10^{-4}	Vinyl chloride monomer	3×10^{-5}
Ti	6×10^{-4}	SOLIDS	
SO ₂	2		
Cl ₂	4×10^{-3}	Zinc mills tailings	2,000
CO	2×10^{-2}	Sludge	6
HCl (mist)	8×10^{-2}	Cd	3×10^{-5}
TiCl ₄	1×10^{-3}	Cr	6×10^{-2}
Vinyl chloride monomer	2×10^{-2}	Cu	3×10^{-3}
Organic mists (organic acids and glycols)	7×10^{-3}	Hg	3×10^{-5}
Benzene	6×10^{-4}	Mn	1×10^{-3}
Xylene	7×10^{-4}	Pb	1×10^{-2}
Hydrocarbons	7×10^{-4}	Se	8×10^{-5}
NO _x	2×10^{-2}	Zn	3×10^{-1}
Flourides	1×10^{-4}	Chlorinated hydrocarbons	2×10^{-2}
		V	1×10^{-1}
		Zr	2×10^{-1}
		Ti	5×10^{-1}

the electricity generation industry in the period 1985 to 2000 (Sec. 12 of Ref. 4). This would require about 500,000 modules per year or a total of 7.5 million modules over the 15-year period; the emissions in Table 2.9 are based on the deployment of 500,000 modules in a year.

2.7.2 Electric Vehicle Applications

The physical configuration of the Zn/Cl_2 battery module for electric vehicle (EV) applications appears quite different from the load-leveling module. The latter contains the chlorine storage volume inside the same case as the electrode stack volume; in the EV battery, these would be placed in separate cases. In addition, the EV battery is long and low, while the load-leveling module has a box-like appearance ($44 \times 44 \times 60$ inches). Despite these differences, the technical characteristics of the two battery modules should be similar and the emissions listed in Table 2.9 also should be applicable to the EV unit. Since the scenario for widespread EV use of Zn/Cl_2 batteries currently is not available, the emissions given in Table 2.9 for 500,000 battery modules per year can readily be modified to accommodate other production levels. Table 2.10 presents materials flow rates and significant effluents for production of one million 50-kWh modules per year.

2.8 IMPACTS ON EXISTING RESOURCES

The impacts of widespread use of Zn/Cl_2 batteries on domestic sources of materials can be seen in Table 2.11. This table is based on an annual production of one million 50-kWh Zn/Cl_2 battery modules and shows the fraction of U.S. materials production required for their manufacture. The major impacts indicated are in the synthetic graphite, titanium, and zinc chloride industries. It is likely that as the Zn/Cl_2 battery design matures, use of titanium will be reduced, and the degree of titanium production expansion implied in the table will not actually be needed. However, it is clear that the U.S. production capabilities for ZnCl_2 will need marked expansion; furthermore, since specialized types of graphite are used in the battery module, the fraction of U.S. graphite production required, as estimated in the table, is probably much too low.

Table 2.9. Estimated Daily Emissions Resulting from Manufacture of 500,000 Zn/Cl₂ Battery Modules per Year†¹ (50 kWh each)

Emission	Amount, kg/day	Emission	Amount, kg/day
AIR		WATER	
Particulates	70	Zn	600
Pb	1	Pb	4
Zn	12	Hg	0.01
Co	0.006	Cd	1
Ni	0.007	Cyanide	1
Cd	0.7	Cu	1
Mn	0.07	As	0.05
As	0.01	Se	0.3
Sb	0.01	Vinyl chloride monomer	0.04
SO ₂	3000		
Cl ₂	6	SOLIDS	
CO	30	Zinc mill tailings	3,000,000
HCl (mist)	100	Sludge	8,000
TiCl ₄	1	Cd	4
Ti	0.8	Cr	80
Vinyl chloride monomer	30	Cu	4
Organic mists (organic acids and glycols)	10	Hg	0.04
Benzene	0.8	Mn	1
Xylene	1	Pb	10
Hydrocarbons	1	Se	0.1
NO _x	30	Zn	4,000
Fluorides	0.1	Chlorinated hydrocarbons	30
		V	100
		Zr	300
		Ti	700

†¹ Assuming 360 days per year of operation.

Table 2.10. Materials Flow Rates and Significant Effluents
from the Zinc/Chloride Battery Cycle
(10⁶-50 kWh modules per year)

Stages and Materials Flow in the Battery Cycle	Air Emissions, kg/day					Water Effluents, kg/day				Solid Effluents, kg/day		
	Pb	As	Cd	VCM	SO ₂	Pb	As	Cd	VCM	Pb	Cd	Cr
Zinc Mining & Milling 7500 MT/day	3	-	0.01	-	-	8	-	-	-	-	-	-
Primary Zinc Production 130 MT/day	0.2	0.03	1	-	6000	0.6	0.1	0.6	-	60	8	0.1
Chlorine Production 140 MT/day	-	-	-	-	-	0.006	-	-	-	30	-	-
Titanium Production 36 MT/day	-	-	-	-	-	-	-	-	-	-	-	150
Graphite Manufacture 190 MT/day	-	-	-	-	-	-	-	-	-	-	-	-
Polyvinylchloride Production 200 MT/day	-	-	-	60	-	-	-	-	0.08	-	-	-
Polyester Resin Mfg. 97 MT/day	-	-	-	-	-	-	-	-	-	-	-	-
Fiber Glass Manufacture 33 MT/day	-	-	-	-	0.7	-	-	-	-	-	-	-
Battery Module Manufacture 2780 50-kWh Modules/day	-	-	-	-	-	-	-	-	-	-	-	-
Total Effluents, kg/day	3	0.03	1	60	6000	9	0.1	2	0.08	90	8	150

Table 2.11. Impact of Zn/Cl₂ Batteries (10⁶ modules per year) on U.S. Domestic Materials Sources

Material	Amount Required, MT/10 ⁶ modules	Percentage of U.S. Annual Production† ¹
Zinc	50,000	11† ²
Chlorine	50,000	0.50
Synthetic graphite	70,000	24† ²
Titanium	10,000	55
Polyvinyl chloride	70,000	2.5
Fiberglass-reinforced polyester	50,000	4.7† ³
Hydrochloric acid	50,000	1.9
Zinc chloride	100,000	470† ²
Magnesium	3,000	2.6
Vinyl chloride monomer	70,000	2.2
Phthalic anhydride	10,000	2.2
Maleic anhydride	7,000	4.2
Propylene glycol	5,000	1.9
Ethylene glycol	4,000	0.20
Styrene monomer	10,000	0.31
Fiberglass	10,000	2.6

†¹ Facts and Figures for the Chemical Industry," Chemical and Engineering News, June 9, 1980.

†² U.S. Department of the Interior, 1977 Minerals Yearbook, Vol. 1, Washington, 1980.

†³ Estimated from propylene glycol production data.

2.9 SUMMARY

1. Emissions from utilization of Zn/Cl_2 battery modules (50 kWh) were estimated for the entire industrial cycle. Among the significant emissions estimated for an assumed production of 1,000,000 battery modules per year were:

- 6 MT SO_2 per day
- 0.06 MT vinyl chloride monomer per day
- 0.2 MT HCl mist per day
- 2×10^{-4} MT benzene per day.

2. The impact on U.S. domestic sources of materials was estimated, and major increases in U.S. production was indicated for the following materials (based on 10^6 battery modules per year):

- 55% increase in titanium production
- 24% increase in synthetic graphite production,
- ~ 500% increase in zinc chloride production.

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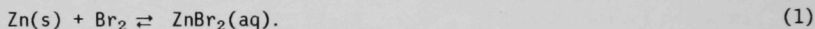
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3. EFFLUENTS FROM THE ZINC/BROMINE BATTERY CYCLE

3.1 INTRODUCTION

3.1.1 Zinc/Bromine Battery Concept

The zinc/bromine battery concept is similar to that of the zinc/chloride battery (Sec. 2.1.1) in that it consists of a zinc electrode, a halogen electrode (in this case, bromine) and an aqueous electrolyte containing the zinc halogen salt (ZnBr_2) in solution. The cell reaction, analogous to the zinc/chloride battery, is:



However, the problems of self-discharge of such batteries due to high solubility of bromine in the ZnBr_2 solution have led to the use of complexing agents to form a polybromide phase. Control of the aqueous phase bromine concentration is attained by this means.^{1,2} The open circuit voltage for the cell is 1.84 V;¹ the zinc/bromine system provides a theoretical energy density of 435 Wh/kg (200 Wh/lb).³

As in the case of the zinc/chloride battery, reduction to practice has required use of a fairly complex battery system for the Zn/Br_2 cell: flowing electrolyte, requiring a pump and valving; membrane/separators; and separate storage reservoirs for the aqueous phase and the bromine complex. Details of these systems are presented in a later section.

3.1.2 Description of a Generic Battery Module

The development of the zinc/bromine battery system is still in its early stages and a definitive design for such a battery module is not yet available. This battery system is currently being studied by Gould, Inc., for utility

load-leveling applications and by Exxon Research and Engineering Company primarily for motive power (EV applications). While the general characteristics of the batteries being developed by these two corporate investigators are similar, there are differences significant enough to influence the results of an effluent estimation such as this one. In the following discussions effluent estimates will be chiefly based on the Exxon battery design proposed for EV applications;¹ since this design is related to a smaller sized battery (~ 20 kWh) the emission values obtained should be quite conservative for load-leveling applications because in the latter case one would expect materials economies in the scale-up from the smaller EV design.

Figure 3.1 shows a schematic drawing of a Zn/Br₂ battery based on the Exxon design.¹ The battery module is constructed almost completely of plastic. The electrodes are fabricated of a conductive carbon plastic arranged in a bipolar configuration and mounted in polypropylene frames containing electrolyte distribution channels. The electrodes are stacked together much like leaves in a filter press and have spacers and separators between each bipolar unit. The terminal electrodes have current collectors imbedded in the plastic with bus bars connected to the current collector tabs.

A 20-kWh EV module would be about 20 in. × 25 in. × 30½ in. high and weigh about 675 pounds. The lower portion of the module contains the reservoirs for the electrolytes; the upper portion contains the battery stacks. The pump and its motor fit into a recess in the bottom of the module. A ribbed plastic cover fits over the entire upper section and bolts to a similarly constructed base tank which comprises the anolyte reservoir.

3.1.3 Module Operational Characteristics

The battery module is a source of direct current electricity with the following capabilities:¹ four battery stacks (52 series-connected cells each) connected in parallel with a cell loading of 75 mAhr/cm²; the average discharge voltage is 1.55 volts. This combination yields a 22-kWh gross energy capability; however, about 10% of this energy would be used by auxiliary systems.

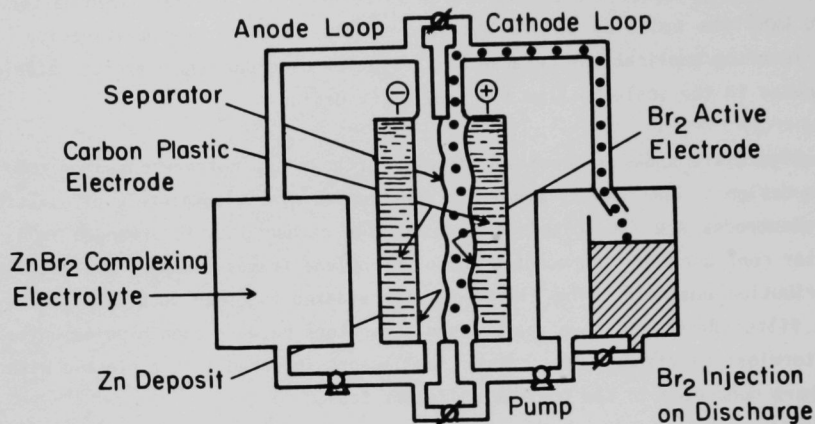


Fig. 3.1. Schematic Diagram of the Zinc/Bromine Circulating Battery. From Exxon Report GRP 882, "Development of a Zinc-Bromine Battery for Motive Power," May 1, 1979.

The voltage for the Zn/Br_2 cell, like that of the Zn/Cl_2 system, is quite flat during the period of discharge. Life-cycle testing of cells¹ has yielded energy efficiencies in the neighborhood of 70%.

During the battery charging process, zinc metal is deposited on the anodes and the bromine evolved at the cathodes reacts with the complexing

agent to form a dense, oil-like phase which separates and is collected in a separate reservoir. During discharge, the bromine complex is recirculated back to the cell and the zinc and bromine react at their respective electrodes to form zinc bromide and release electrical energy.

3.1.4 Module Input Materials

The major materials expected to be used in manufacturing 20-kWh Zn/Br₂ battery modules are estimated to be:^{1,4}

<u>Material</u>	<u>kg/kWh</u>
ZnBr ₂	4.5
Battery complexing agent† ¹	0.14
Carbon black	0.54
Polypropylene	3.4
PVC	0.11
Teflon	0.01

†¹ Currently N-ethyl, N-methyl morpholinium bromide.

It should again be emphasized that these material inputs are for a still-developing battery system and it is likely that changes will occur as the module design matures. However, effluent estimates based on this composition are probably conservative.

3.2 PRIMARY PRODUCTION OF INPUT MATERIALS

3.2.1 Zinc

A discussion of estimated effluents from mining and milling of zinc areas and primary zinc production was presented in Section 2.2.1 for the Zn/Cl₂ battery cycle; the same values are applicable here and the reader is referred to that earlier section for the estimated effluents.

3.2.2 Bromine

Bromine in the U.S. is produced chiefly from well brines containing a few tenths of a percent of bromine as salts. The process utilizes chlorine and steam to convert the salt into a crude bromine, which is subsequently purified by distillation.⁵ The wastes from the process (spent brine and neutralized process waters) are returned to their sources. Bromine leakage is nil.⁵ However, about 500 kg H_2SO_4 , 540 kg chlorine, and 250 kg NaOH are required for production of a metric ton of purified bromine. Estimates of the effluents resulting from manufacture of these materials for use in bromine production are given in Table 3.1. The values in table are based on results for chlorine production presented in Section 2.2.2 and other sources.^{5,6} Only gaseous emissions have been considered for sulfuric acid production; the solid and liquidborne wastes from the process are not hazardous⁵ and the quantities involved in the battery cycle are minor compared to those from the sulfuric acid industry as a whole.

3.2.3 Zinc Bromide

Little literature information on zinc bromide manufacture was found. A reasonable production approach would be direct bromination of zinc powder followed by filtration, evaporation, and final drying of the product. By analogy with the production of zinc chloride (Sec. 2.2.4), the small effluent releases from such a process will be disregarded here. About 0.3 MT of zinc and 0.7 MT of bromine are required for production of a metric ton of $ZnBr_2$.

3.2.4 Carbon Black

Carbon blacks are chiefly produced through incomplete pyrolysis of fuel oil or natural gas. The furnace process, which accounts for most of the U.S. production of carbon black,⁶ involves injection of the fuel into a reactor along with a limited amount of air; the combustion gases are then rapidly cooled by water sprays and the carbon black is removed from the gases chiefly via bag filters.

Table 3.1. Estimated Effluents Associated
with Bromine Manufacture

Effluent	Amount, kg/MT Br
AIR	
Chlorine	3×10^{-3}
Carbon monoxide	4×10^{-2}
Sulfuric acid mist	2×10^{-1}
SO ₂	1
WATER	
TSS	1.7×10^{-1}
Pb	2×10^{-5}
SOLIDS	
Total solids	~ 2
Pb solids	1×10^{-1}
Chlorinated hydrocarbons	2×10^{-1}

Estimated effluents⁶ for carbon black production are presented in Table 3.2. Waterborne and solid wastes should be minimal and are not considered here.

3.2.5 Polypropylene

Effluents from manufacture of polypropylene have been discussed in an earlier document in this series (ANL/ES-90, Sec. 2.4.1)⁷ and details of the polymerization of propylene into polypropylene may be found there. Estimates of effluents from the polypropylene manufacturing process are given in Table 3.3.

3.2.6 Polyvinyl Chloride

Estimates of the effluents related to manufacture of polyvinyl chloride have been presented earlier in Section 2.2.7 of this report. The same values are applicable here and the reader is referred to that earlier section for the estimated emissions.

Table 3.2. Estimated Effluents
Associated with Carbon Black
Manufacture

Effluent	Amount, kg/MT carbon black
AIR† ¹	
Particulates	1.1
CO	2.2
Hydrocarbons	0.3
H ₂ S	0.016
WATER† ²	
Wastewater	Negligible
SOLIDS	
Solids	Negligible

†¹ From Ref. 6.

Table 3.3. Estimated Effluents
Associated with Polypropylene
Manufacture

Effluent	Amount, kg/MT polypropylene
AIR† ¹	
Particulates	2×10^{-2}
Hydrocarbons	1.8×10^{-3}
WATER† ²	
TSS	0.23
SOLIDS	
Sludge (dry weight)† ³	5

†¹ Based on data in Ref. 6.

†² Based on the best available technology economically achievable value in Ref. 8.

†³ Based on mean of data in Ref. 8.

3.2.7 Battery Complexing Agent

The battery complexing agent (BCA) currently considered for use in reducing the degree of bromine dissolution in the electrolyte is N-ethyl, N-methyl morpholinium bromide. The major synthetic step in the manufacture of the complexing agent is the formation of the N-disubstituted morpholine. However, the major intermediates in the production of these compounds--ethylene, oxygen, and HCl--are produced in such large quantities that the effects of morpholine production on their overall environmental effluents are negligible.

There appears to be no effluent information in the literature for production of the BCA compound itself; however, examination of the reactions involved in these synthetic processes indicate that a probable source of emissions would be hydrogen chloride produced during the condensation of dichlorodiethyl ether to form the morpholine ring. If one assumes that the HCl is disposed of, rather than utilized for other chemical processing, we can estimate that

on the order of 0.2 MT of HCl/MT of BCA would need to be neutralized and disposed of. The neutralized products would not be hazardous and their disposal via plant effluent water should cause no problems. We shall, conservatively, assume that some release of the HCl via acid mist could occur and that control technology⁶ would reduce this release to about 0.01 kg/MT BCA. It should be reiterated that this is probably an overestimate of what would be emitted in a well-designed chemical plant.

3.2.8 Teflon

Teflon, polytetrafluoroethylene, constitutes about a tenth of a percent of the input materials to the battery module (see Sec. 3.2.4). Its use is primarily in O-ring seals and it is likely that more advanced designs will eliminate much of the use of this very expensive plastic. Since Teflon is used in very small quantities in the battery module and its continued use in this application probably will be reduced, we will not consider here effluents from Teflon manufacture.

3.3 BATTERY MANUFACTURE

A flow sheet for the manufacture of 2000 20-kWh zinc/bromine batteries per day is presented in Figure 3.2; it is based on information developed for the Exxon battery system.¹ Admittedly, this manufacturing process is at the conceptual design stage and estimates of effluents from such a scheme are clearly very nebulous at this time.

The bipolar electrodes are to be fabricated by extrusion and rolling of the carbon plastic mix; this is followed by injection molding of polypropylene frames around the electrode block. These production processes result in little loss;⁹ most of the excess material from the process would probably be reused. The solid plastic wastes that do result would probably be disposed of by means of incineration rather than by landfill burial. The same situation probably applies to separator fabrication as well.

In the interior cell assembly process, the electrodes and separators are combined into an assembly of 52 cells; the edges are heat-sealed or glued.

Heat-sealing would provide the least likelihood of additional emissions and here we shall assume that the interior cell assembly system utilizes this approach.

Battery stack assembly involves combining the interior cell assemblies with collectors and associated hardware; the end product is an assembly of four stacks (each containing 52 cell assemblies) connected in parallel. The fabrication of the collectors used in this step is similar to that for the bipolar electrode fabrication. The system assembly step combines the various plumbing, control, and pump components with the battery stack assembly inside the case to produce the 20-kWh battery module. These steps are mechanical in nature and should result in no significant effluents. However, the electrolyte is added at this step and it is likely that the mixing and loading of the electrolyte will probably result in some minor spillage. There are no spillage data available for this system, so we shall assume that about 0.5% (by volume) of the electrolyte is spilled and enters the plant sanitary sewage system. This would amount to about 0.02 kg of ZnBr_2 per kWh of the battery module. This material probably ends up in the sludge product from the waste treatment facilities (about 0.6×10^{-2} kg of zinc per kWh of battery as solids and the 1.4×10^{-2} kg of bromide per kWh in the liquid). If the cost of zinc bromide were high enough, one could make use of retention tanks to salvage the spillage.

3.4 NORMAL OPERATION

Outside of possible evolution of small quantities of hydrogen on charging the battery system,¹ there are no significant environmental releases expected during normal operation of the zinc/bromine battery module.

3.5 RECYCLING

The philosophy of design for the Exxon zinc/bromine battery module is based on utilization of an inexpensive, readily replaceable, battery stack. The remainder of the battery system would continue to be used, including the electrolyte.¹ It is likely that the major aspects of a recycling effort would be involved in recovery of zinc and bromine from the old electrolyte and disposal of the plastic components via incineration. However, estimation of emissions from such processes at this time is not practicable.

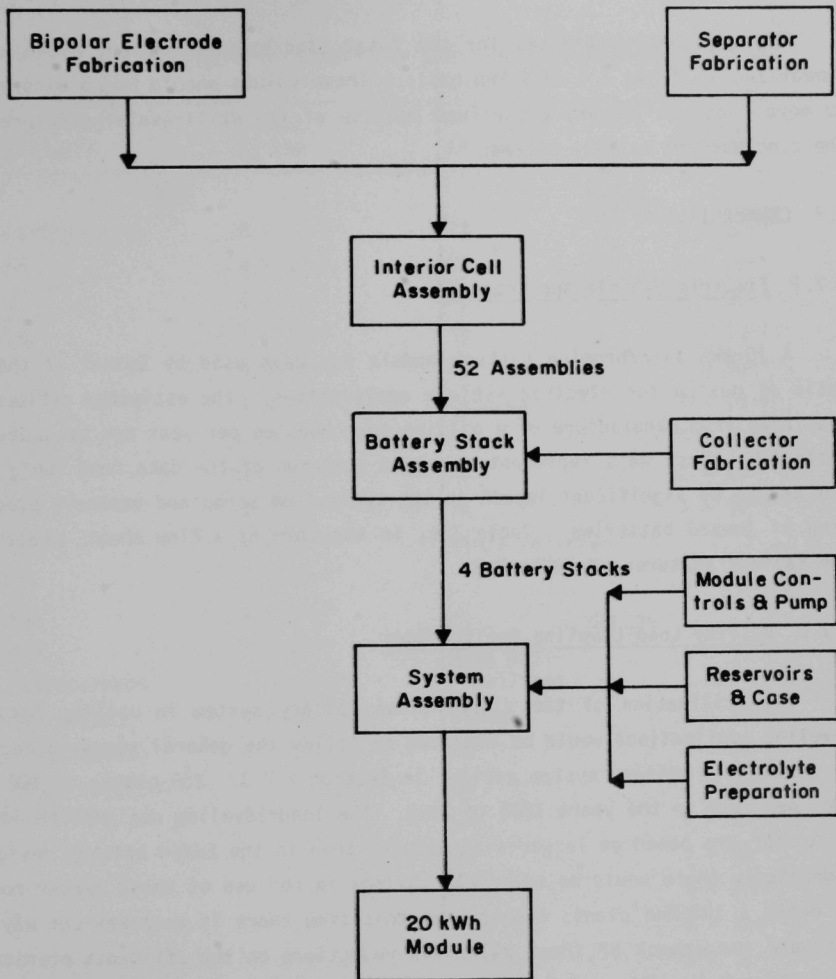


Fig. 3.2. Flow Sheet for Zinc/Bromine Battery Manufacture. After Exxon Report GRP 882, "Development of a Zinc-Bromine Battery for Motive Power," May 1, 1979.

3.6 TOTAL BATTERY CYCLE

The effluents estimated for the total zinc/bromine battery cycle are summarized in Table 3.4 on a kWh basis. These values should be considered as no more than preliminary guidelines because of the still-evolving nature of the zinc/bromine battery system.

3.7 COMMERCIALIZATION

3.7.1 Electric Vehicle Applications

A 20-kWh zinc/bromine battery module has been used by Exxon¹ as their basis of design for electric vehicle applications. The estimated effluents resulting from manufacture of a million such modules per year are presented in Table 3.5; these data represent merely a scale-up of the data from Table 3.4 and assume no significant impact on the cycle from scrap and recovery processing of junked batteries. Table 3.6, in the form of a flow sheet, presents the salient features of Table 3.5.

3.7.2 Utility Load-Leveling Applications

The utilization of the zinc/bromine battery system in utility load-leveling applications would be expected to follow the general scenario outlined for the $ZnCl_2$ battery system earlier in Section 2.7.1: 250 plants of 100 MWh each per year in the years 1985 to 2000. The load-leveling designs considered by Gould² are based on larger-size modules than in the Exxon battery design.¹ Undoubtedly there would be materials savings in the use of these larger modules to build a 100-MWh plant; however, at this time there is no clear-cut way to estimate the impact of these materials reductions on the effluents predicted in Section 3.6. Thus, the estimated load-leveling battery industry effluents presented here in Table 3.7 are certainly overestimates of what probably would be emitted by a mature industry, since they are based on the small module estimates of Table 3.4. Nevertheless, the estimates do provide a conservative basis for analysis of the system until better data become available.

Table 3.4. Estimated Effluents for the Zinc/Bromine Battery Cycle

Effluent	Amount, kg/kWh	Effluent	Amount, kg/kWh
AIR		WATER	
Particulates	8×10^{-4}	TSS	7×10^{-3}
Pb	4×10^{-5}	Zn	1×10^{-4}
As	4×10^{-7}	Pb	7×10^{-5}
Cd	1×10^{-5}	Hg	3×10^{-7}
Sb	4×10^{-7}	Cd	1×10^{-5}
Co	1×10^{-7}	Cyanide	3×10^{-5}
Zn	2×10^{-4}	Cu	4×10^{-5}
Ni	1×10^{-7}	As	1×10^{-6}
Mn	1×10^{-6}	Se	1×10^{-5}
SO ₂	6×10^{-2}	Vinyl chloride monomer	5×10^{-8}
CO	1×10^{-3}	SOLIDS	
Cl ₂	1×10^{-5}		
H ₂ S	9×10^{-6}	Zinc mill tailings	52
Hydrocarbons	2×10^{-4}	Sludge	8×10^{-2}
HCl (mist)	1×10^{-6}	Cd	7×10^{-5}
H ₂ SO ₄ (mist)	6×10^{-4}	Cr	1×10^{-6}
Vinyl chloride monomer	4×10^{-5}	Cu	9×10^{-5}
		Hg	7×10^{-7}
		Mn	3×10^{-5}
		Pb	8×10^{-4}
		Se	2×10^{-6}
		Zn	1×10^{-2}
		Chlorinated hydrocarbons	6×10^{-4}

Table 3.5. Estimated Effluents from Manufacture of a Million 20-kWh Battery Module Units per Year†¹

Effluent	Amount, kg/day	Effluent	Amount, kg/day
AIR		WATER	
Particulates	40	TSS	400
Pb	2	Zn	6
As	2×10^{-2}	Pb	5
Cd	6×10^{-1}	Hg	2×10^{-2}
Sb	2×10^{-2}	Cd	6×10^{-1}
Co	6×10^{-3}	Cyanide	2
Zn	10	Cu	2
Ni	6×10^{-3}	As	6×10^{-2}
Mn	6×10^{-2}	Se	6×10^{-1}
SO ₂	3000	Vinyl chloride monomer	3×10^{-3}
CO	70		
Cl ₂	6×10^{-1}	SOLIDS	
H ₂ S	5×10^{-1}	Zinc mill tailings	3×10^6
Hydrocarbons	10	Sludge	4×10^3
HCl (mist)	6×10^{-2}	Cd	4
H ₂ SO ₄ (mist)	30	Cr	6×10^{-2}
Vinyl chloride monomer	2	Cu	5
		Hg	4×10^{-2}
		Mn	2
		Pb	50
		Se	1×10^{-1}
		Zn	600
		Chlorinated hydrocarbons	30

†¹ Assumes 360 days per year.

Table 3.6. Materials Flow Rates and Significant Effluents from the Zinc/Bromine Battery Cycle (10⁶ 20-kWh modules per year)

Stages and Materials Flow in the Battery Cycle	Air Emissions, kg/day						Water Effluents, kg/day				Solid Effluents, kg/day	
	Pb	As	Cd	CO	SO ₂	VCM	Pb	Cd	As	VCM	Pb	Cd
Zinc Mining & Milling 4000 MT ore/day	2	--	0.006	--	--	--	4	0.6	--	--	--	--
Primary Zinc Production 72 MT/day	0.1	0.02	0.6	--	3000	--	0.06	--	0.06	--	30	4
Bromine Production 94 MT/day	--	--	--	6	200	--	0.003	--	--	--	20	--
Carbon Black Manufacture 31 MT/day	--	--	--	60	--	--	--	--	--	--	--	--
Polyvinylchloride Manufacture 6 MT/day	--	--	--	--	--	2	--	--	--	0.003	--	--
Polypropylene Manufacture 190 MT/day												
Battery Module Manufacture 2780 20-kWh modules/day												
Total Effluents, kg/day	2	0.02	0.6	70	3000	2	5	0.6	0.06	0.003	50	4

Table 3.7. Estimated Effluents from Manufacture of 250 Utility Load-Leveling Battery Plants per Year†¹ (100-MWh capacity each)

Effluent	Amount, kg/day	Effluent	Amount, kg/day
AIR		WATER	
Particulates	50	TSS	500
Pb	2	Zn	8
As	2×10^{-2}	Pb	6
Cd	8×10^{-1}	Hg	2×10^{-2}
Sb	2×10^{-2}	Cd	8×10^{-1}
Co	8×10^{-3}	Cyanide	2
Zn	10	Cu	2
Ni	8×10^{-3}	As	8×10^{-2}
Mn	8×10^{-2}	Se	8×10^{-1}
SO ₂	4000	Vinyl chloride monomer	3×10^{-3}
CO	90		
Cl ₂	8	SOLIDS	
H ₂ S	6×10^{-1}	Zinc mill tailings	4×10^6
Hydrocarbons	10	Sludge	5×10^3
HCl (mist)	8×10^{-2}	Cd	5
H ₂ SO ₄ (mist)	40	Cr	8×10^{-2}
Vinyl chloride monomer	3	Cu	6
		Hg	5×10^{-2}
		Mn	2
		Pb	60
		Se	1×10^{-1}
		Zn	800
		Chlorinated hydrocarbons	40

†¹ Assumes 360 days per year.

3.8 IMPACTS ON EXISTING RESOURCES

The impact of production of a million 20-kWh zinc/bromine battery modules per year on existing resources can be seen in Table 3.8. The major effect--expansion of manufacturing capabilities--are clearly indicated for the following important input materials: bromine, zinc bromide, and intermediate organic reagents required for the production of the battery complexing agent (BCA). Since BCA is not an article of commerce, an industrial production capability would also have to be developed; however, since morpholine (its parent compound) is manufactured in the U.S. at a level of about 10,000 MT per year,¹¹ the technology for its manufacture is available. The quantities of other materials listed in Table 3.8 probably could be accommodated by existing U.S. industrial production capabilities.

3.9 SUMMARY

Effluents were estimated for the zinc/bromine battery cycle at production levels of a million 20 kWh modules per year and 250 utility load-leveling plants per year of 100 MWh capacity each. The significant effluents found were:

- ~ 4MT SO₂ per day,
- ~ 3×10^{-3} MT vinyl chloride monomer per day, and
- ~ 6×10^{-4} MT H₂S per day.

The impacts of such widespread deployment of zinc/bromine battery systems on U.S. production capabilities were also estimated. The major production expansions required would be for bromine, zinc bromide, and the battery complexing agent plus its production intermediates.

Table 3.8. Impact of Manufacture of Zinc/Bromine Batteries
on Existing Resources (10⁶ 20-kWh modules/year)

Resource	Amount Required, MT/10 ⁶ modules	Percentage of U.S. Annual Production
Zinc	26,000	6.2† ¹
Bromine	64,000	28† ²
Chlorine	35,000	0.32† ²
Zinc bromide	90,000	*† ³
Carbon black	11,000	0.73† ²
Polypropylene	68,000	3.9† ²
Polyvinyl chloride	2,200	0.08† ²
Battery complexing agent	2,800	*† ⁴
Chlorethanol	2,200	17† ⁵
Teflon	200	2.2† ⁶

†¹ U.S. Department of the Interior, "1977 Minerals Yearbook, Vol. I," Washington, 1980.

†² Ref. 10, 1979 production values.

†³ No production data found: however, a reasonable production estimate would be of the order of 30,000 MT Per year.

†⁴ Not a commercial chemical.¹

†⁵ Manufacturing Chemists Association, "Chemical Statistics Handbook, 7th Ed.," Washington, 1971.

†⁶ U.S. International Trade Commission, "Synthetic Organic Chemicals, U.S. Production and Sales 1978," USITC Publication 10001, 1979.

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4. DISPERSION OF EFFLUENTS

4.1 GENERAL DESCRIPTION

Site-specific dispersion of effluents is presented in this document for source-receptor distances of up to 100 km.

The pollutants of concern are lead (Pb), cadmium (Cd), sulfur dioxide (SO_2), particulates (from the same source as SO_2), sulfuric acid mist, and vinyl chloride. The industries of concern are those that produce appreciable amounts of one or more of these pollutants. They are zinc mining and milling, zinc smelting and refining, and polyvinyl chloride (PVC) manufacture. Other industries in the battery cycle are as yet nonexistent (zinc/halogen battery manufacture) or do not emit much of the pollutants of concern (case material manufacture for ZnCl_2 batteries, titanium manufacture, vinyl chloride production, etc.)(Secs. 2 and 3).

For each industry two sites have been chosen for study. The sites represent a reasonably wide range of variation of some of the relevant parameters over all the sites for the industry of interest. The choices are limited by such factors as availability of meteorological data for nearby sites, plant production and emission data, etc.

For each industrial site chosen the dispersion is calculated using pollutant emission rates for actual plant production levels (Zn mine-mills) or for plant capacities (Zn smelter-refiners and PVC manufacture). The results can be appropriately scaled to obtain that fraction of a plant's output which is attributable to the scenario production of ZnCl_2 and ZnBr_2 batteries.

The scenario production of ZnCl_2 batteries requires an annual production of 25,000 metric tons of zinc and 35,000 metric tons of PVC. For ZnBr_2 batteries the corresponding figures are 26,000 metric tons and 2200 metric tons (Secs. 2 and 3).

The dispersion is calculated based on detailed emission data available for plants as they have been operating during the past few years. Estimates may therefore be conservative since plants operating in the future may use more advanced pollution control technology and thus have reduced emission factors compared to plants operating at present or during the past few years.

For each industrial site chosen, the near-field dispersion of pollutants is calculated using an advanced Gaussian dispersion model (The ISC model).¹ Meteorological data from nearby National Weather Service stations are used for the site in question. Such data include hourly measurements of wind speed and direction, atmospheric stability class, and ambient air temperature. Plume rise due to momentum and buoyancy as a function of downwind distance is included for stack emissions. Stack tip downwash is also included and the model can accommodate multiple point, line, area or volume sources. The model can account for the effect of gravitational settling, by use of a settling velocity, and dry deposition by use of a reflection coefficient, and accepts particle-size distributions with corresponding distributions of the settling velocity and reflection coefficient. The time-dependent decrease in pollutant concentrations due to chemical transformation, etc., is provided for by inclusion of an exponential decay factor. The model enables one to calculate both atmospheric concentrations and dry deposition rates. Further details for the concentrations and deposition rates are given in Appendix A.

The output data obtained here for each industrial site chosen and its respective pollutants consist of isopleths for seasonal average ground-level atmospheric concentrations and deposition rates. For each pollutant and site, two sets of output data, which represent different meteorological conditions and resultant population exposures, are given in graphical form as isopleths of atmospheric concentrations and of deposition rates.

4.2 SOURCE DATA

4.2.1 Zinc Mining and Milling

Zinc mines and mills can be divided into two groups--those that mine zinc in conjunction with, or as a by product of, lead mining, and those that mine

zinc ore. Those associated with lead mining are in Missouri and Idaho and the others are mainly in Tennessee plus a large mine-mill complex in New Jersey. The two sites chosen for further analysis are the Buick Mine in Iron County, Missouri, and the Sterling Mine in Sussex County, New Jersey. These two mines ranked 1 and 2 respectively in zinc production in 1979 with production of ore containing about 35,000 MT and 31,100 MT of zinc.² (The amount of production of the Buick mine was obtained by analysis of the data for 1979 in the U.S. Minerals Yearbook.) The Buick Mine is located in a rural area about 130 km from St. Louis and the Sterling Mine is in northern New Jersey about 70 km from New York City.

Table 4.1 gives the relevant source data for these two mine-mills. The values for plant areas are estimates obtained by converting the approximate known area of a lead smelter³ to a square. The annual plant production in metric tons of zinc is for the year 1979, a year of low total U.S. production.² Plant production fluctuates widely because of such factors as demand for zinc, the percent zinc in the ore mined, etc. In 1976 the Buick Mine produced 55,300 MT of zinc.⁴

The meteorological data for St. Louis and for Bridgeport, Conn., will be used for the Buick and Sterling Mines, respectively. Even though these are not onsite data, they are assumed to be sufficiently characteristic of conditions at the Buick and Sterling Mine sites to be used for dispersion modelling.

Fugitive emissions are the main type of emission from zinc mine-mills. A release height of five meters is assumed in view of the fact that fugitive emissions arise from ore transport, crushing, and storage, and from building vents.

The emission rates are calculated as follows: emission factors of 2.0 g/kg ore produced and 1.0 g/kg ore produced for ore transport, storage and ore crushing and grinding, respectively,⁵ are combined to give an emission factor of 3.0 g/kg ore produced. In 1979, the Buick Mine processed 1.8×10^6 MT of ore. The 31,100 MT of zinc produced by the Sterling Mine was assumed to come from ore averaging 4.3% zinc content.² A 50% reduction in emissions due to good housekeeping was assumed.⁶ ("Good housekeeping" is a term used in the

Table 4.1. Source Data for Zinc Mine-Mills

Parameter	Values for Mine-Mill	
	Buick Mine	Sterling Mine
Location	Iron Co., MO	Sussex Co., NJ
Mine-mill area (m ²)	400 × 400	400 × 400
Plant production (MT/yr, 1979)	35,000	31,100
Meteorological data site (distance (km) from mine)	St. Louis (130)	Bridgeport (125)
Emission release height (m)	5	5
Fugitive emission rate (g/sec)		
Particulates	86	34
Pb	6.67	0.068
Cd	0.018	9.0×10^{-4}

Particle Size Distribution

Diameter (μ)	Wt %	Settling Velocity, cm/sec.	Reflection Coefficient
<0.95	59.7	~0	0.5
0.95-1.9	5.8	0.024	0.5
1.9 -4.6	11.6	0.12	0.5
>4.6	22.9	1.1	0.78

literature to mean activities that reduce fugitive dust emissions, such as the wetting of ore piles or the covering of ore-transport vehicles.) Combining these values gives the particulate emissions given in the table. The lead and cadmium emission rates are calculated by assuming that the Buick Mine ore contains 7.8% lead² and a Cd/Pb ratio of 0.00273, which is typical for Missouri lead mines (Sec. 2). The lead and cadmium emissions for the Sterling mine are calculated assuming a lead content of 0.2% in the zinc ore⁵ and an emission factor for Cd of 0.91×10^{-3} kg/MT zinc in the ore.⁷ For the above it is also assumed that the content of Pb and Cd in the particulates emitted is the same as in the ore.

The emissions are divided into four particle-size distribution classes. These classes with the corresponding weight percentages are the values actually measured in the ore storage bin area of a Missouri primary lead smelter³ and thus should be reasonable approximations for the values applicable to the zinc mine-mill fugitive dusts.

The gravitational settling velocities were calculated from the expression

$$V_s = \frac{\rho g d^2}{18\mu} \quad (1)$$

where ρ is the particle density, g = gravity acceleration (980 cm/sec^2), μ is the absolute viscosity of air ($1.83 \times 10^{-4} \text{ g/(cm sec)}$), and d is the mass median diameter. d is given by

$$\left(\frac{d_1^3 + d_1^2 d_2 + d_1 d_2^2 + d_2^3}{4} \right)^{1/3} \quad (2)$$

where d_1 and d_2 are the respective lower and upper bounds of the particle-size category.¹

Here ρ was taken to be 3.67 g/cm^3 .³ For the $<0.95\mu$ category in the table $d_1 = 0$ and for the >4.6 category d was arbitrarily set equal to 10 microns. The reflection coefficient, Υ , for this last category was taken from the relationship between V_s and Υ given by Dumbauld et al.⁸ For the remaining categories the reflection coefficient was arbitrarily chosen equal to 0.50.

This value which is midway between 0, no surface reflection, and 1.0, complete surface reflection, also represents a reasonable compromise between the limitations of a model which treats the effects of dry deposition using reflection coefficients and the more reasonable use of deposition velocities.

4.2.2 Zinc Smelting and Refining

As was the case for the mine-mills, the zinc smelters can be divided into two groups--those that use pyrometallurgical methods and those that use electrolytic methods. There are five electrolytic smelters in operation and two pyrometallurgical smelter sites, one at Monaca, Pennsylvania, and the other at Palmerton, Pennsylvania. The Monaca site was closed at the end of 1979, and the smelting part of the Palmerton site was closed at the end of 1980. The site at Monaca will be reopened in September, 1981, to process ore from a recently found zinc ore body in New York.⁹

Because closure of these sites depends on the demand for zinc as well as other factors, these sites may be utilized in the future if demand for zinc picks up. As a result, one pyrometallurgical smelter site (the New Jersey zinc plant at Palmerton) and one electrolytic smelter site (the ASARCO site at Corpus Christi) are chosen for an analysis. The Palmerton site is chosen instead of the Monaca site because of the availability of site-specific emission data.^{10,11}

Table 4.2 gives the relevant source data for the sites. The plant areas are assumed to be square with the area equal to that given for a lead smelter.³ The areas are relevant for fugitive emissions which are considered to be area emissions. Plant capacities are used instead of plant production rates. The reason is that production fluctuates appreciably from year to year. Also, use of plant capacities gives emission rates of pollutants under maximum plant utilization.²

Meteorological data from the Wilkes Barre-Scranton Airport and for San Antonio are used for the respective Palmerton and Corpus Christi sites. As in the case of the zinc mine-mills, it is assumed that these data are sufficiently characteristic of conditions at the smelter sites to be used for dispersion modelling.

Table 4.2. Source Data for Zinc Smelter-Refiners

Parameter	Values for Smelter Refiners				
	New Jersey Zinc		ASARCO		
Location	Palmerton, PA		Corpus Christi, TX		
Type	Pyrometallurgical (Vertical Retort)		Electrolytic		
Plant area (m ²)	400 × 400		400 × 400		
Plant capacity (MT/yr)	109,000		98,000		
Meteorological data site	Wilkes Barre-Scranton, PA		San Antonio, TX		
Distance to plant (km)	62		97		
Fugitive emission release height (m)	5		5		
Stack parameters					
Height (m)	75		75		
Top inside diameter (m)	5.3		1.6		
Exit gas temperature (°C)	200		200		
Exit gas velocity (m/sec)	10		10		
Pollutant emission rates (g/sec)	<u>Fugitive</u>	<u>Stack</u>	<u>Fugitive</u>	<u>Stack</u>	
Particulates	11.4	88.1	5.00	--	
Pb	0.224	3.45	0.099	--	
Cd	0.015	5.11	0.0081	--	
SO ₂	--	121	--	35	
H ₂ SO ₄ (mist)	--	0.43	--	0.39	
Particle-size distribution					
Data					
Fugitive emissions--see Table 4.1					
Stack emissions					
Particle diameter	<u>Mass Fraction</u>			Gravita- tional Settling Velocity, cm/s	Reflec- tion Coeff.
	Particulates	Cd	Pb		
<2μ	0.49	0.64	0.60	0	0.5
>2μ	0.51	0.36	0.40	0.12	0.5
	<u>Summer</u>	<u>Winter</u>			
SO ₂ inverse lifetimes (sec ⁻¹)	3.6 × 10 ⁻⁶	1.33 × 10 ⁻⁶			

Since fugitive emissions arise from ore storage, transport, and handling, and from building leaks, the emissions heights for both sites are taken to be the same as for zinc mine-mills.

The stack parameters for the pyrometallurgical smelter are estimated as follows: the estimated gas flow up the stack from the sinter and vertical retort from a plant producing 109,000 MT Zn/yr is about 13 m³/sec.⁵ An exit velocity of 10 m/sec was estimated from literature data relating wind speeds to atmospheric stability classes and recommended exit velocities.¹² The diameter is determined from the flow and velocity. The temperature is an average of the range of temperatures for exit gases from sintering⁵ and is also an average of temperatures of gases through an electrostatic precipitator (Ref. 13 p. 140). The stack height is an estimated value.¹¹

Fugitive emissions occur at both types of smelter. Uncontrolled fugitive emission factors from several steps in the pyrometallurgical process are given in the literature.⁵ The factors can be combined with literature values of the amounts of Zn, Pb, Cd, and As in the product as it moves through the smelter¹⁴ to get emission factors per metric ton zinc for each pollutant. These are summed over the process steps, then reduced by a factor of 2 to account for a 50 percent reduction from good housekeeping practices⁶ and multiplied by an appropriate conversion factor to give the entries in Table 4.2. The conversion factor changes emission factors to emission rates.

For electrolytic smelters, uncontrolled fugitive emission factors are 0.27 g/kg ore concentrate for the roasting step⁵ and 1.5 g/kg roasting product for the remaining steps.¹⁴ If one assumes that the fugitive emissions have the same composition as the ore concentrate and roasting product, then the above emission factors yield the source fugitive emission rates of pollutants as given in the table. Again a 50% control factor was used.

Stack emissions of particulates, Pb, and Cd from the New Jersey zinc pyrometallurgical smelter are taken from direct measurements of stack effluents from the sintering process, the coking step, and the vertical retort at the plant. Only the sinter emissions are controlled (by a cyclone and electrostatic precipitator).¹⁰ Although each process at the smelter is served by a

separate stack, the plant is modelled here as though it had one large stack. Also the particulate and Pb emission factors in kg/MT Zn summed over all three steps are normalized by multiplying by the ratio of the actual Cd emission factor (1.48 kg/MT Zn) to the sum of the separate Cd emission factors for each of the three steps (2.48 kg/MT Zn). This normalization is necessary because of the complex flow pattern and recycling of zinc-bearing materials in the plant.¹⁰ This also makes modelling the stack emissions as coming from three stacks (as is the case) quite difficult and is therefore one of the reasons why the emissions are assumed to come from one large stack.

Carrying out the above normalization gives particulate, Pb, and Cd emission factors of 25.5 kg/MT Zn, 1.00 kg/MT Zn, and 1.48 kg/MT Zn, respectively. All these values are multiplied by a conversion factor to give the emission rates in the table.

Most of the SO₂ emissions arise from the roasting process. These emissions are controlled by passage through a sulfuric acid plant. The remaining emissions come from the sinter operation (pyrometallurgical smelter only). Assumption of a flow of 1.95 m³/sec exhaust gas per MT/hr of ore concentrate moving through the sinter process and a new source performance standard of at most 0.065 volume percent SO₂ in the exhaust gas¹⁵ gives an SO₂ emission factor from the sinter process of 24 kg/MT Zn.

For the sulfuric acid plant an emission factor of 6.7 kg SO_x/MT H₂SO₄ can be derived from the total estimated SO_x emissions in 1978 from H₂SO₄ plants of 2.2×10^5 MT¹⁶ and a total H₂SO₄ use in 1978 of 3.29×10^7 MT.² The assumptions that SO_x = SO₂ and that 1100 kg SO₂ are produced per MT zinc,¹⁵ give an SO₂ emission factor of 11.2 kg SO₂/MT Zn produced from the H₂SO₄ plant. Combination of this with the sinter SO₂ emissions and multiplying by an appropriate conversion factor gives the SO₂ emission rate in the table for the Palmerton site.

The above estimates of SO₂ emissions are subject to much uncertainty. For instance the New Source Performance Standards¹⁵ for SO₂ emissions from H₂SO₄ production is 2 kg SO₂/MT H₂SO₄. This is a factor of 3.3 lower than the factor used here. The literature data for sinter operations are so variable that calculated SO₂ emission factors differ by factors of 20 or more.

The H_2SO_4 (mist) arises as a stack emission from the sulfuric acid plant. It is included here for the sake of completeness, since the main health effect of SO_2 considered in Section 6 arises from the conversion of SO_2 to SO_3 and sulfates. The source emission rate was calculated by use of the New Source Performance Standard emission factor of 0.075 kg H_2SO_4 mist/MT H_2SO_4 . This is a conservative estimate in that the use of either fiber mist eliminators or electrostatic precipitators reduces emissions to less than 0.075 kg/MT.¹⁵ Conversion of this to an emission factor/MT Zn and multiplying by the plant capacity gives the value in the table.

Emissions from the electrolytic zinc smelter are mainly fugitive emissions with controlled particulate emission factors of 0.25 kg/MT Zn for the roasting operation and 1.36 kg/MT Zn for the other operations. These values are calculated from the literature values for uncontrolled emission factors for ore concentrate^{5,14} and use a 50 percent control factor⁶ and a 55 percent zinc content in the ore concentrate.¹⁴ The following assumptions are also used: The Pb, Cd, and As compositions of the fugitive emissions are the same as those of the feed to the roasting operations. Also, for the electrolytic emissions, the compositions are the same as those of the feed to the electrolytic operations. These assumptions and emission factors, along with an appropriate conversion factor for plant capacity, give the values in the table.

The stack emissions from the electrolytic plant are taken to be those from the H_2SO_4 plant associated with the roasting operation.² Except for the stack diameter the stack parameters are taken to be equal to those for the pyrometallurgical smelter. The stack diameter is calculated from the assumption that offgases from the roasting operation flow at a rate sufficient to contain 10% (vol.) SO_2 at 200°C.¹⁴ Also 1100 kg SO_2 are generated/Mt zinc.¹⁵ The sulfuric acid mist emission rate is calculated in the same manner as is the value for the Palmerton site.

The particle-size distribution for fugitive emissions from both sites was taken to be the same as that used for the zinc mine-mill. The source of these data is actual measurements in the ore storage bin area of a lead smelter.³ Thus, it should be representative of the distributions of particle sizes for

at least some of the sources of fugitive emissions at a zinc smelter. The gravitational settling velocities and reflection coefficients are taken to be the same values as were used for the zinc mine-mills.

Experimental data are available on the particle size in the stack emissions from the pyrometallurgical smelter.¹⁰ This work divided the emissions into two size groups, the respirable part with diameters $<2\mu$, and the non-respirable part with diameters $>2\mu$. It was found that 49 wt.% of the stack particulate emissions were in the $<2\mu$ group. However, 60 wt.% of the lead and 64 wt.% of the cadmium were in the $<2\mu$ group. Thus, considerable fractionation of the volatile metals toward the smaller size particles was found. These fractions are given in Table 4.2. Gravitational settling velocities and reflection coefficients for the stack emissions were determined in the same manner as the values for fugitive emissions given in Table 4.1.

After being emitted into the air SO_2 slowly oxidizes to form SO_3 , sulfates, and sulfuric acid. Since these are of interest from a health standpoint, it is necessary to take account of this transformation. This is done here by assumption of a first order process which gives an exponential decay term. The SO_2 transformation coefficients were taken to be $3.06 \times 10^{-6} \text{ sec}^{-1}$ in the summer and fall and $1.33 \times 10^{-6} \text{ sec}^{-1}$ in the winter and spring.¹⁷

4.2.3 Polyvinyl Chloride Manufacture

Table 4.3 gives data for two plants which polymerize vinyl chloride monomer (VCM) into polyvinyl chloride (PVC). The two plants, the Conoco plant at Oklahoma City and the Firestone plant at Perryville, Maryland, were chosen from the 35 plant sites on the basis of close proximity to meteorological data sites and population density immediately surrounding the site. The Conoco plant is in the same city as the meteorological data site. The population density around the Conoco plant is appreciable, 280 people/km². It is lower around the Firestone plant, 56 people/km².¹⁸

Fugitive emissions arise from such sources as transfer operations, valve and pump seal leaks, opening equipment for maintenance and inspection, etc. Site-specific data for many of the 35 plants have been combined, in a litera-

Table 4.3. Source Data for Polyvinyl Chloride Manufacture

Parameter	Values for Manufacturers	
	Conoco	Firestone Tire
Site location	Oklahoma City, OK	Perryville, MD
Meteorological site	Oklahoma City, OK	Baltimore, MD
Distance from plant (km)	0	50
Plant capacity (MT/yr)	99,800	104,300
Plant area (m ²)	130 × 130	130 × 130
Fugitive VCM emissions		
Emission rate (g/s)	50.0	25.4
Emission height (m)	2	2
Stack VCM emissions		
Emission rate (g/s)	66.0	33.6
Emission height (m)	16	18
Stack diameter (m)	0.55	0.55
Discharge temperature (°C)	77°	77°
Discharge velocity (m/sec)	5.6	5.6
Inverse lifetime (sec ⁻¹)	5.8 × 10 ⁻⁶	5.8 × 10 ⁻⁶

ture report,¹⁸ into data for a representative plant. In such a plant 43 percent of emissions are ascribed to fugitive sources and 57 percent to process sources. The VCM emission factors for each plant are multiplied by the above factors and stack emission factors of VCM.¹⁸ The fugitive emission height was taken to be 2 m.

Process emissions arise from such sources as tank, centrifuge, and condenser vents, etc.¹⁸ These emissions are assumed here to come out of one stack. The stack height for the Firestone plant is an average value for that plant. The height for the Conoco plant is an average determined for the representative plant. The remaining stack parameters are obtained as averages for processes in xylene manufacture.¹⁹ These parameters should be reasonable approximations for PVC manufacture, which is also a petrochemical process.

The VCM fugitive and stack emission rates are calculated using the VCM emission factors, 36.7 kg VCM/MT PVC for the Conoco plant and 17.8 kg VCM/MT PVC for the Firestone tire plant.¹⁸ However, these values were obtained in 1974 before industry changes were made in response to the recognition that VCM

is a carcinogen. According to the literature "EPA standards on vinyl chloride emissions require a 95% or better reduction in atmospheric vinyl chloride emissions".¹⁸ The regulations are complex. For several process steps in PVC manufacture released gases must contain at most 10 ppm VCM. For one process step for one type of PVC product, emissions are limited to 2g VCM per kg PVC (41 FR 46559 10/21/76; 42 FR 29005 6/7/77). Other emission factors apply to other process steps.

After being released to the atmosphere, VCM, which is a fairly reactive chemical, undergoes transformation. In particular, it contributes to the formation of smog.¹⁸ In common with many other smog-producing chemicals, the main agent which attacks VCM is thought to be the OH radical. The 1/e lifetime of VCM against OH attack, which can be estimated from the reaction rate constant for OH attack and the concentration of OH radicals, is about two days.²⁰ This gives an inverse lifetime of $5.8 \times 10^{-6} \text{ sec}^{-1}$, which is used here.

4.3 RESULTS

4.3.1 Atmospheric Concentrations

Use of the source data and model which were discussed in Section 4.2 allows one to calculate and plot atmospheric ground-level concentration isopleths for each pollutant and site of interest. An averaging period of three months was chosen and calculations were limited to a region 200 km \times 200 km centered on the site. As a result, for each pollutant-site combination, four graphs were generated, one each for spring (March-May), summer (June-August), fall (September-November) and winter (December-February).

Results are given in Figures 4.1 through 4.36. Two of the four seasonal isopleth graphs are presented here for each pollutant site combination. The two chosen are those that look the least alike. This is done to show the effect of different seasonal meteorological conditions on the dispersion. The contour intervals are chosen to represent data at a level of detail appropriate for the health analysis. The numbers on the contour lines give the pollutant ground-level atmospheric concentrations in micrograms per cubic meter (SO_2 ,

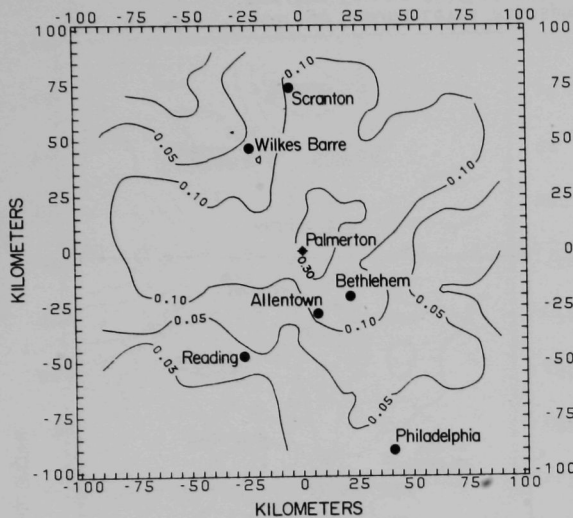


Figure 4.1. SUMMER

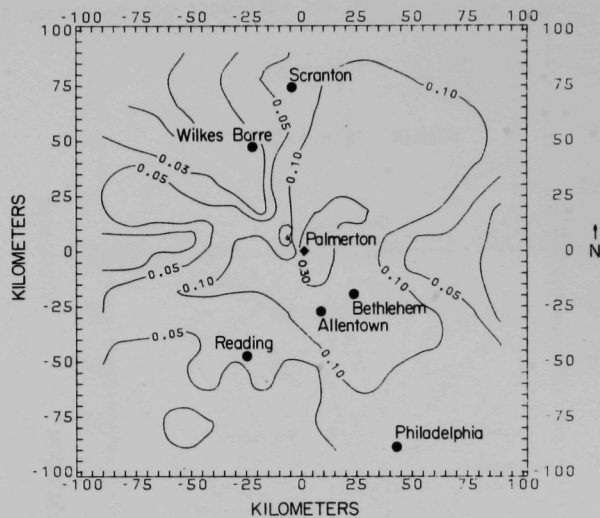


Figure 4.2. WINTER

Average Ground-Level Atmospheric Concentration Isopleths for SO_2 for the Palmerton Site. The plant site is at the center of the graph. Coordinate distances in kilometers from the plant site at (0,0). North is at the top of the graph and is denoted by N. The contour lines are labelled with atmospheric concentrations in $\mu\text{g}/\text{m}^3$.

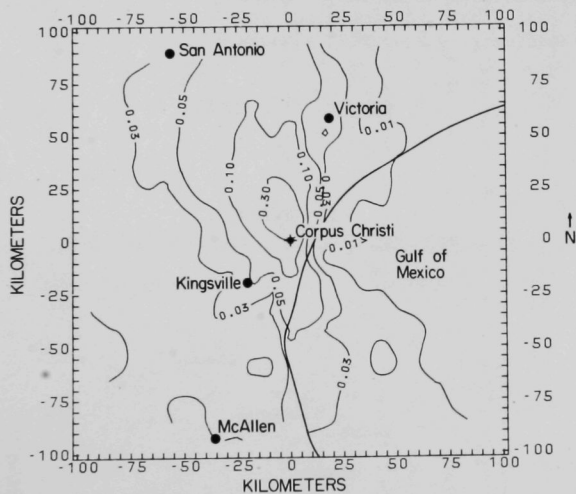


Figure 4.3. SUMMER

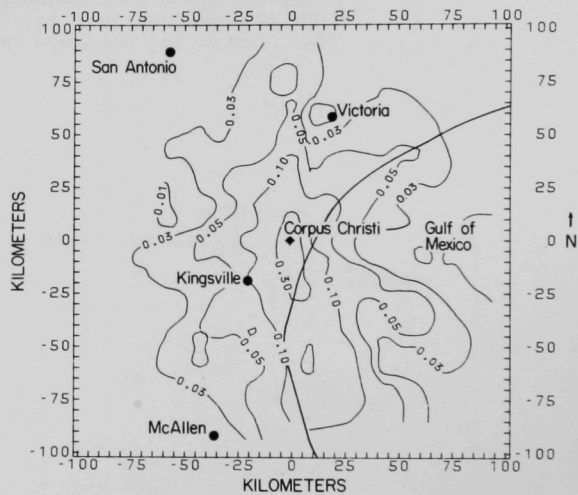


Figure 4.4. WINTER

Average Ground-Level Atmospheric Concentration Isopleths for SO_2 for the Corpus Christi Site. See Figures 4.1 and 4.2 caption for details.

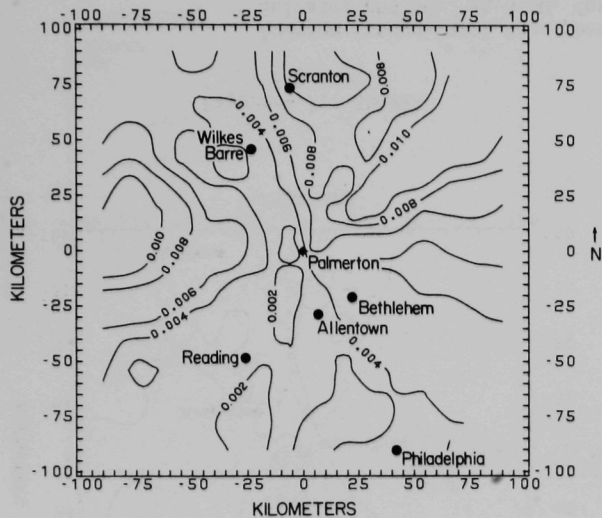


Figure 4.5. SUMMER

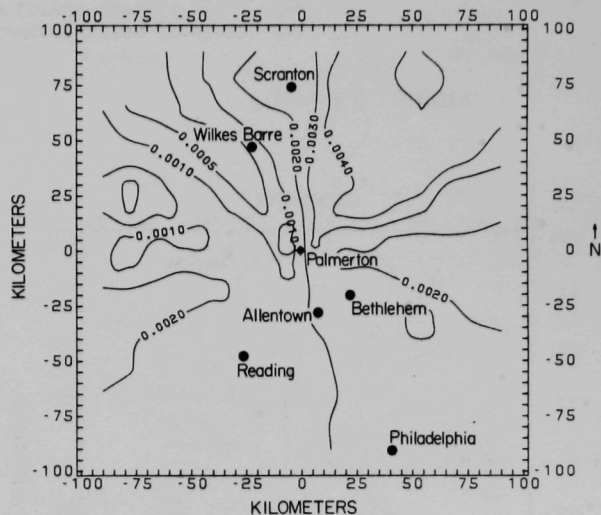


Figure 4.6. WINTER

Average Ground-Level Atmospheric Concentration Isopleths for Sulfates and SO_3 , as H_2SO_4 for the Palmerton Site. See Figures 4.1 and 4.2 caption for details.

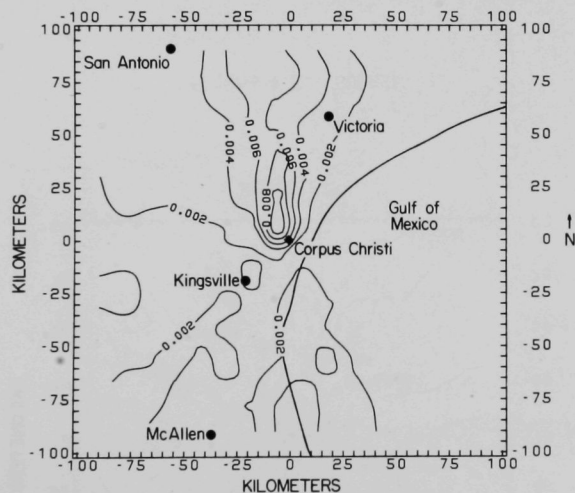


Figure 4.7. SUMMER

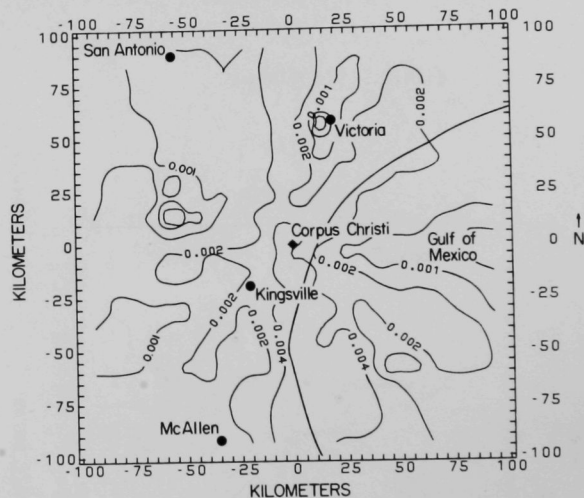


Figure 4.8. WINTER

Average Ground-Level Atmospheric Concentration Isopleths for Sulfates and SO_3 , as H_2SO_4 for the Corpus Christi Site. See Figures 4.1 and 4.2 caption for details.

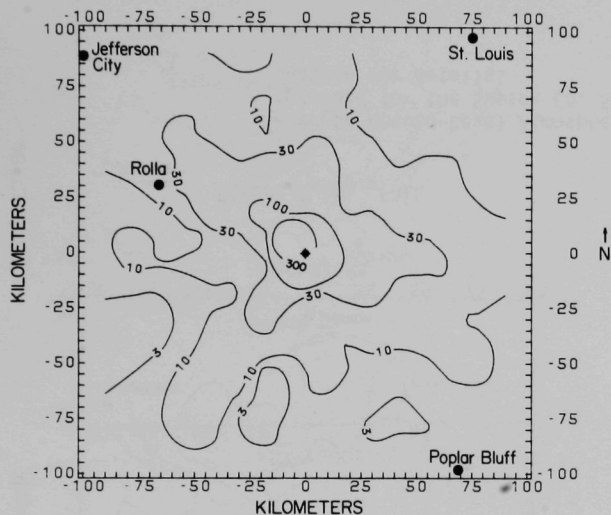


Figure 4.9. SUMMER

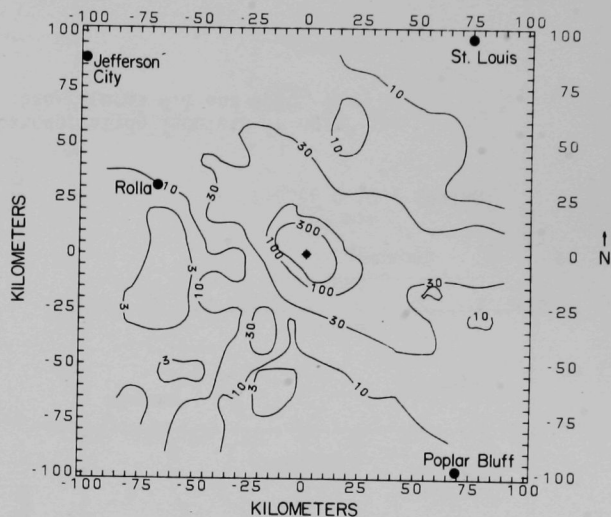


Figure 4.10. WINTER

Average Ground-Level Atmospheric Concentration Isopleths in nanograms per cubic meter (ng/m^3) for Lead for the Iron Co. Site. See Figures 4.1 and 4.2 caption for details.

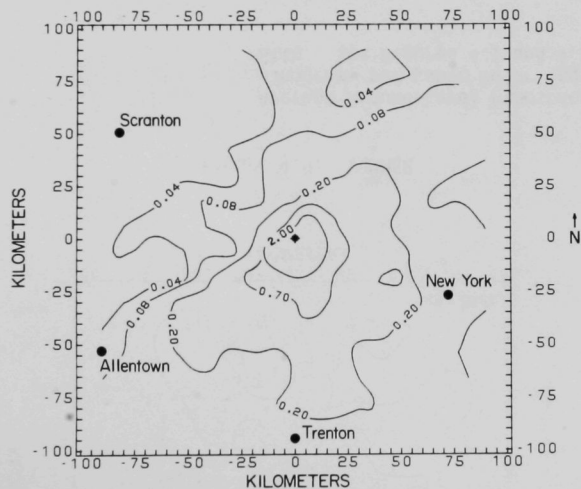


Figure 4.11. FALL

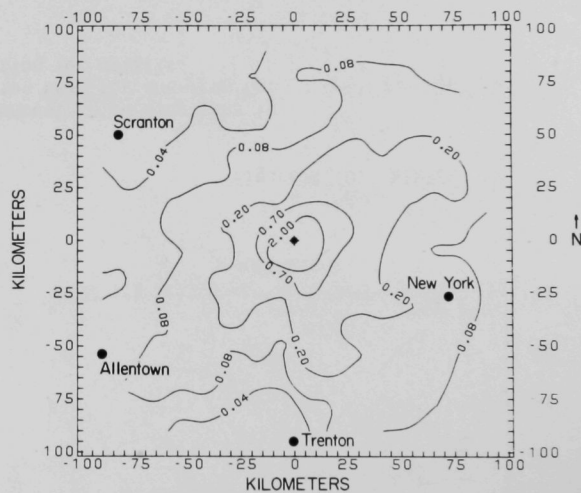


Figure 4.12. SPRING

Average Ground-Level Atmospheric Concentration Isopleth in ng/m^3
for Lead for the Sussex Co. Site. See Figures 4.1 and 4.2
caption for details.

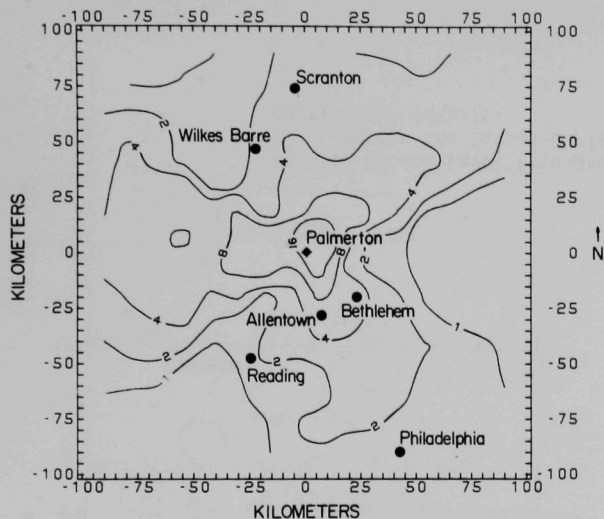


Figure 4.13. FALL

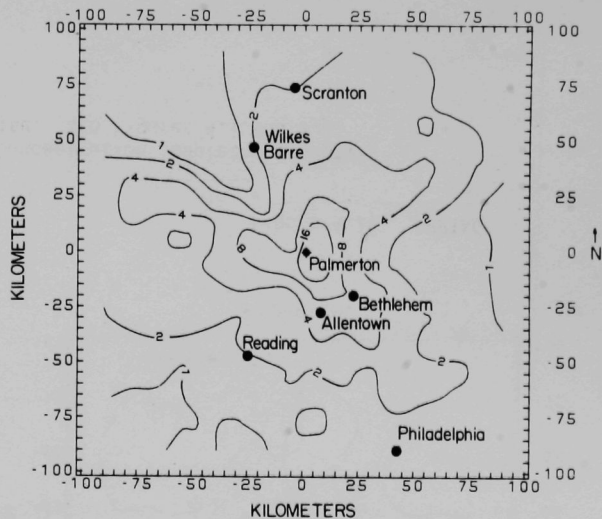


Figure 4.14. SPRING

Average Ground-Level Atmospheric Concentration Isopleth in ng/m^3 for Lead for the Palmerton Site. See Figures 4.1 and 4.2 caption for details.

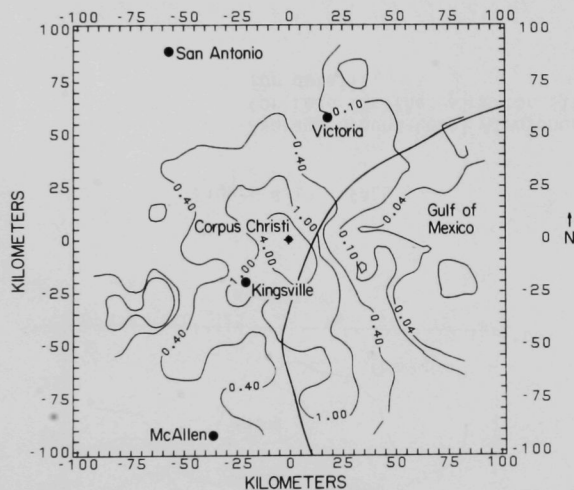


Figure 4.15. FALL

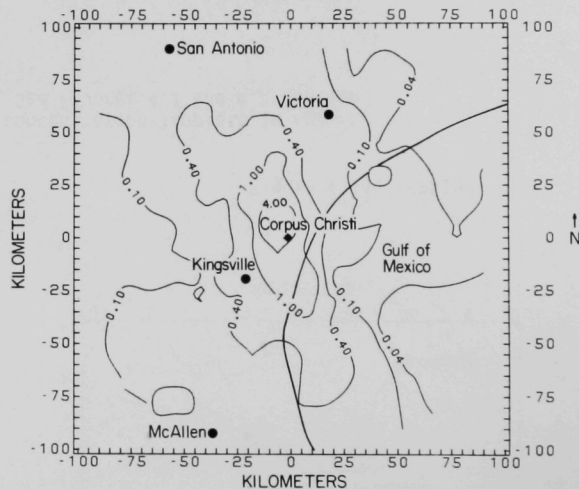


Figure 4.16. SPRING

Average Ground-Level Atmospheric Concentration Isopleths in ng/m³ for Lead for the Corpus Christi Site. See Figures 4.1 and 4.2 caption for details.

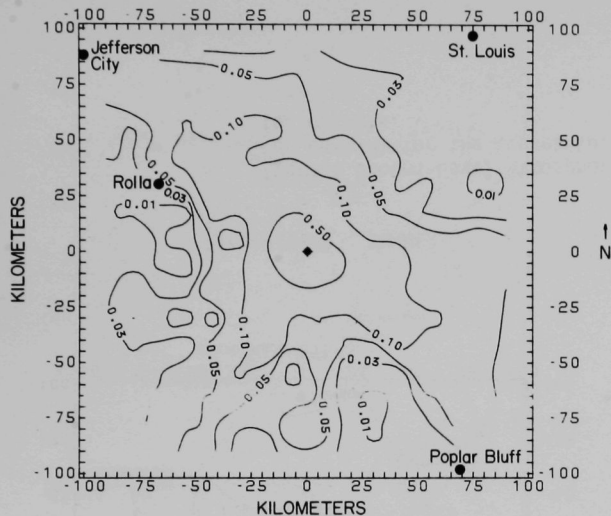


Figure 4.17. FALL

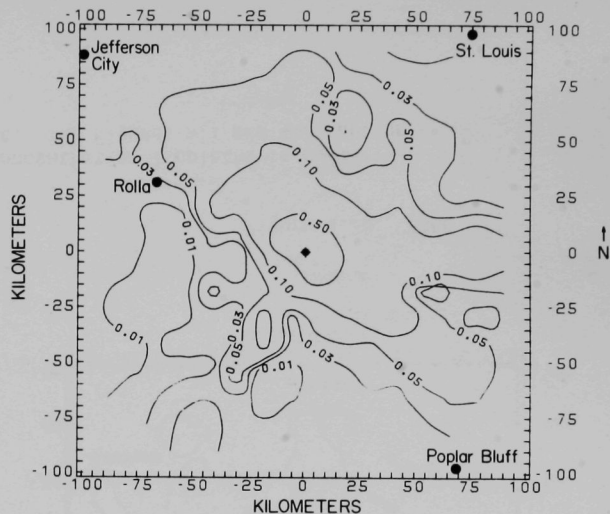


Figure 4.18. WINTER

Average Ground-Level Atmospheric Concentration Isopleths in ng/m^3 for Cadmium for the Iron Co. Site. See Figures 4.1 and 4.2 caption for details.

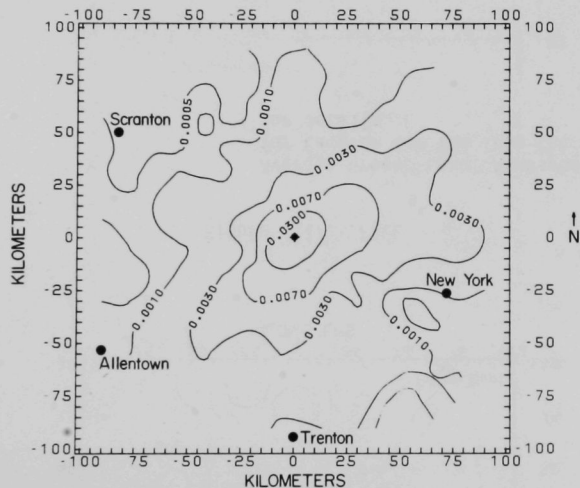


Figure 4.19. SUMMER

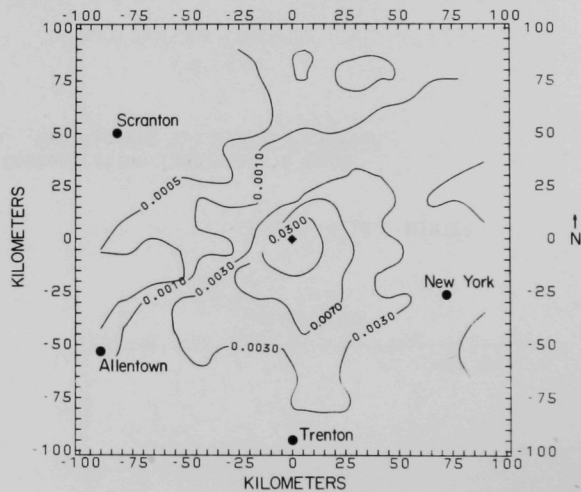


Figure 4.20. FALL

Average Ground-Level Atmospheric Concentration Isopleths in ng/m^3 for Cadmium for the Sussex Co. Site. See Figures 4.1 and 4.2 caption for details.

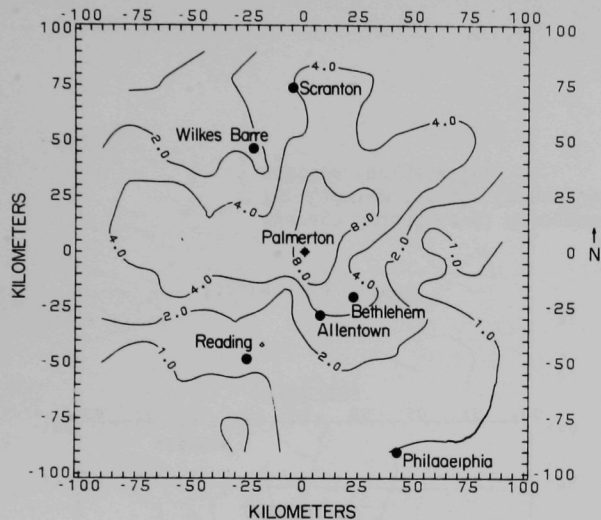


Figure 4.21. SUMMER

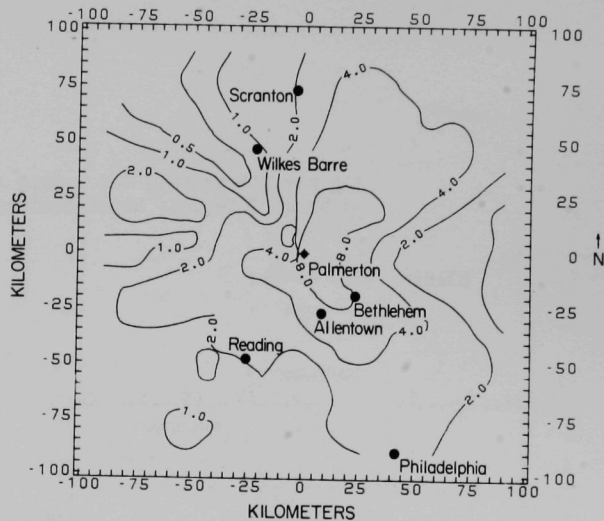


Figure 4.22. WINTER

Average Ground-Level Atmospheric Concentration Isopleths in ng/m³ for Cadmium for the Palmerton Site. See Figures 4.1 and 4.2 caption for details.

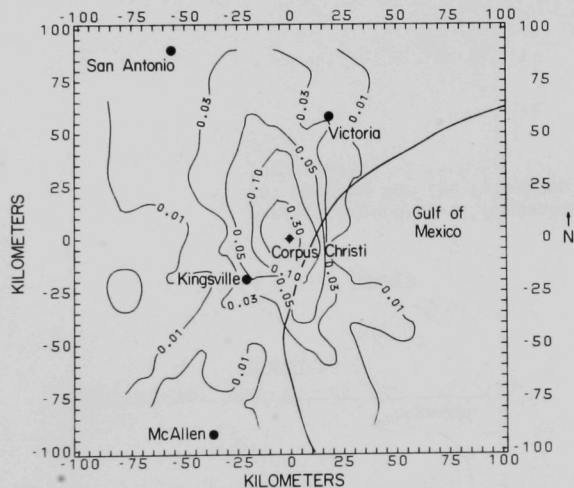


Figure 4.23 SUMMER

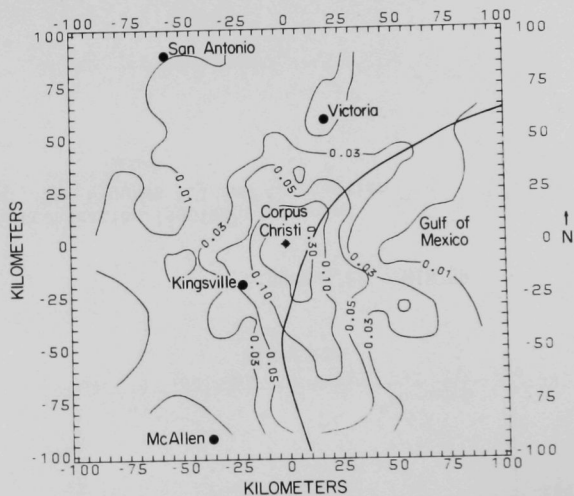


Figure 4.24 WINTER

Average Ground-Level Atmospheric Concentration Isopleths in ng/m^3 for Cadmium for the Corpus Christi Site. See Figures 4.1 and 4.2 caption for details.

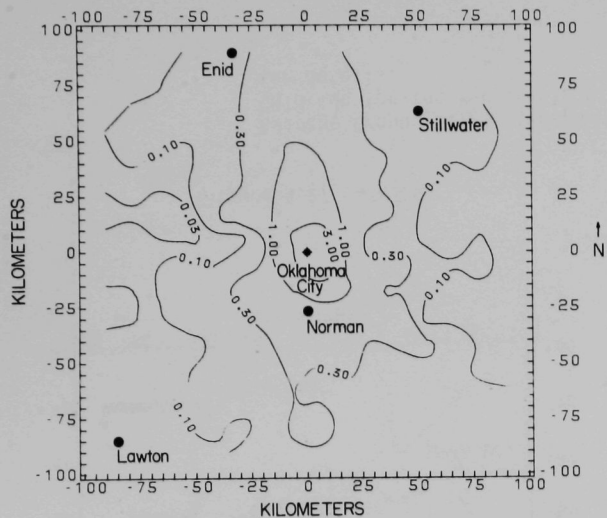


Figure 4.25 WINTER

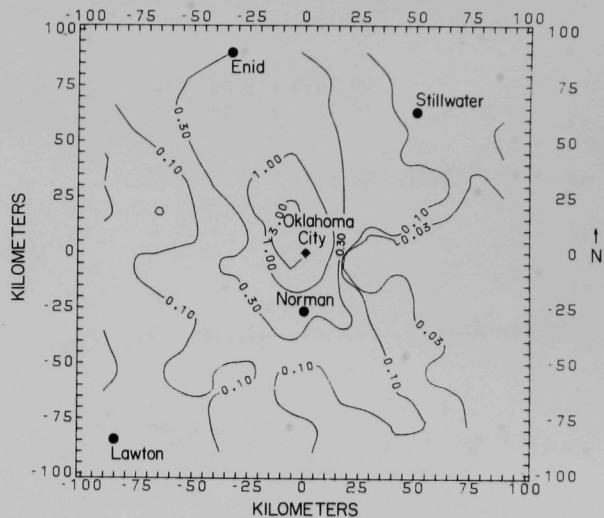


Figure 4.26 SUMMER

Average Ground-Level Atmospheric Concentration Isopleths for Vinyl Chloride for the Oklahoma City Site. See Figures 4.1 and 4.2 caption for details.

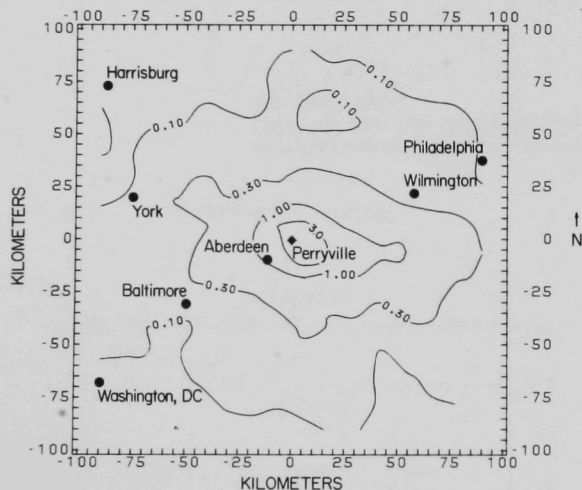


Figure 4.27 WINTER

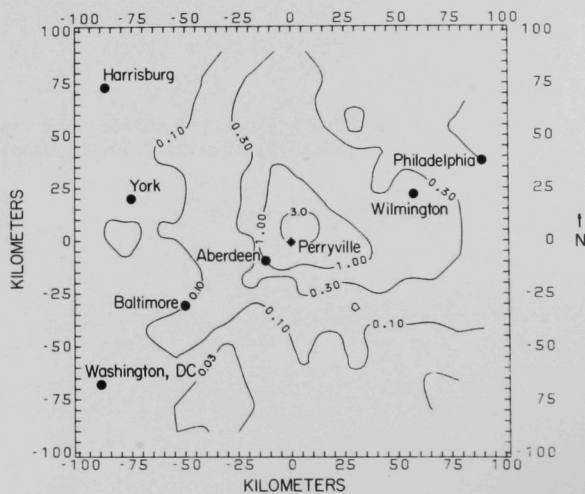


Figure 4.28 SUMMER

Average Ground-Level Atmospheric Concentration Isopleths for Vinyl Chloride for the Perryville Site. See Figures 4.1 and 4.2 caption for details.

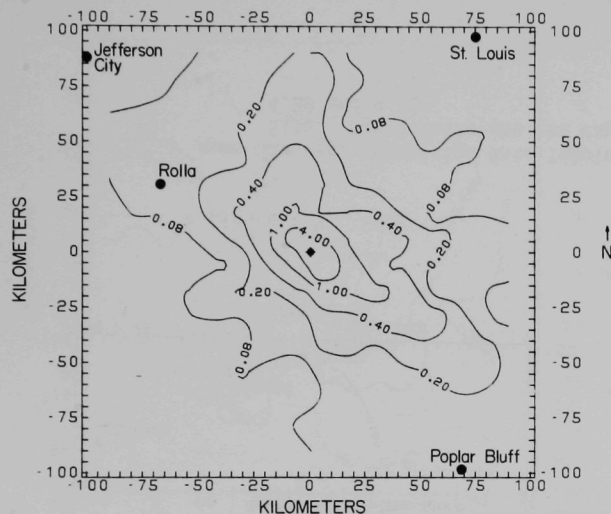


Figure 4.29 WINTER

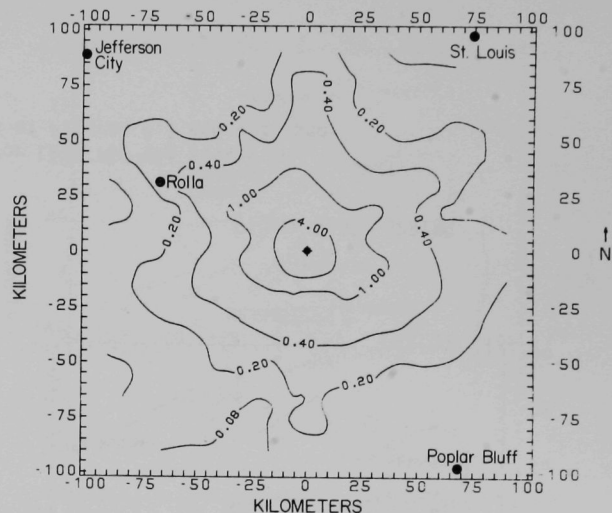


Figure 4.30 SUMMER

Average Deposition Rate Isopleths for Lead for the Iron Co. Site. The numbers on the contour lines give the deposition rates in nanograms per square meter per second. For further details see the Figures 4.1 and 4.2 caption.

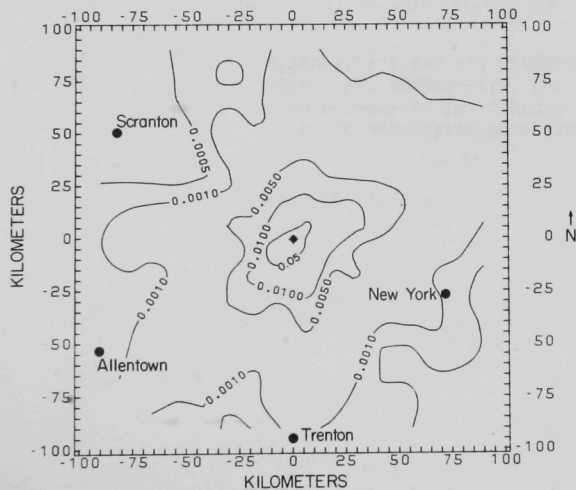


Figure 4.31 FALL

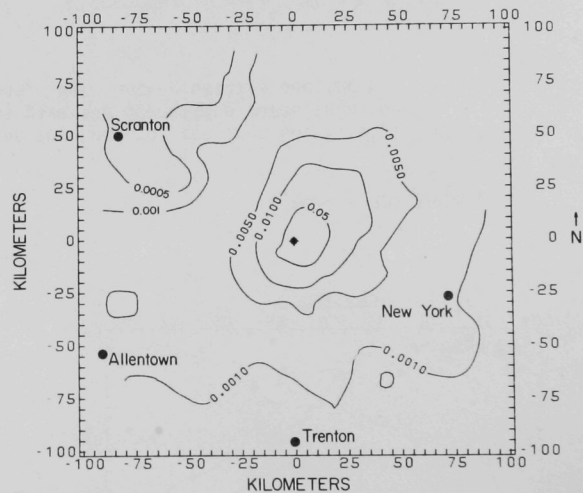


Figure 4.32 SPRING

Average Deposition Rate Isopleths for Lead for the Sussex Co. Site. For details see the captions of Figures 4.1 and 4.2, and 4.29 and 4.30.

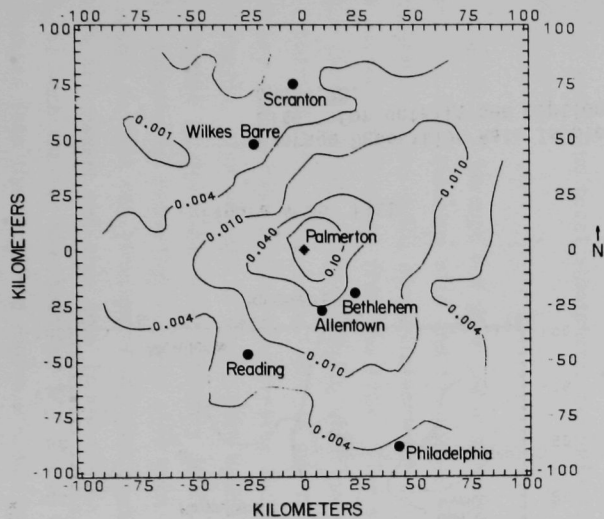


Figure 4.33 FALL

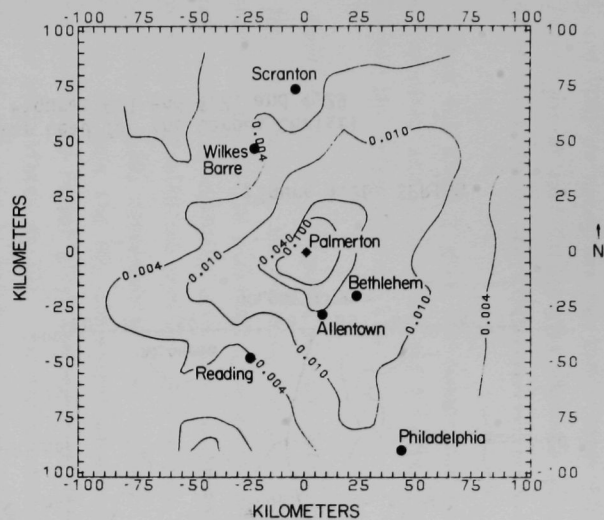


Figure 4.34 SPRING

Average Deposition Rate Isopleths for Lead for the Palmerton Site. For details see the captions of Figures 4.1 and 4.2, and 4.29 and 4.30.

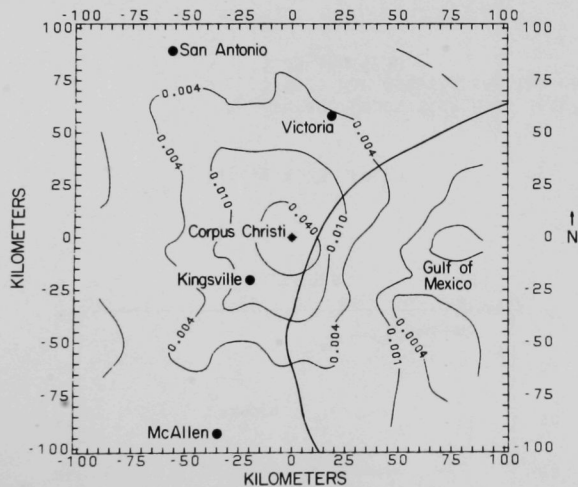


Figure 4.35 FALL

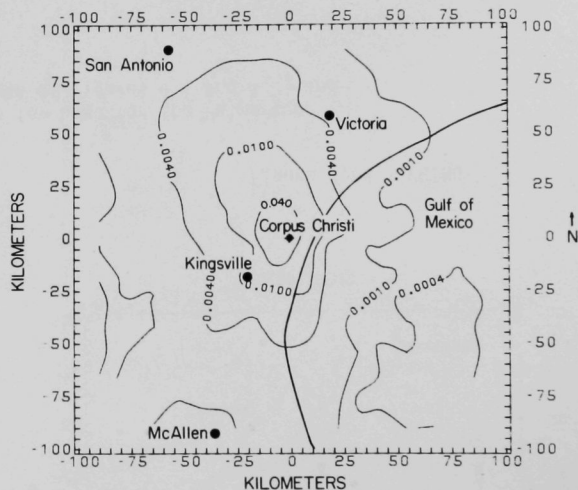


Figure 4.36 SPRING

Average Deposition Rate Isopleths for Lead for the Corpus Christi Site. For details see captions of Figures 4.1 and 4.2, and 4.29 and 4.30.

H₂SO₄ and VCM) or nanograms per cubic meter (Pb and Cd). The numbers along the four sides of each figure give distance in kilometers. The plant site is at the center (0,0) of the figure.

Figure 4.1 and 4.2 give the summer and winter SO₂ isopleths for the Palmerton site, and Figures 4.3 and 4.4 give the summer and winter SO₂ isopleths for the Corpus Christi site.

From the health standpoint sulfate concentration in the air is of interest. For the zinc smelting and refining industry sulfates are generated mainly by oxidation of the sulfur dioxide in the air after it is emitted from the smelter. A small amount of sulfuric acid mist is also emitted directly from the acid plant associated with the smelter. The sulfate concentrations are calculated as equivalent H₂SO₄ concentrations as follows: at each receptor point the difference between the SO₂ concentration calculated with and without the exponential decay factor gives the amount of SO₂ in micrograms per cubic meter converted to sulfates or SO₃. (In the presence of water or water vapor, SO₃ becomes sulfuric acid.) Multiplication by 98/64, the ratio of the molecular weights of H₂SO₄ and SO₂, and addition of the H₂SO₄ concentration from direct emission gives the total atmospheric concentration of H₂SO₄ equivalent at the receptor point.

Figures 4.5 through 4.8 give the resultant summer and winter H₂SO₄ isopleths for the Palmerton site and the Corpus Christi site. Unlike the SO₂ concentrations, the H₂SO₄ concentrations for the Palmerton site show an increase with increasing distance from the site. (The effect is less evident for the Corpus Christi site, as the SO₂/H₂SO₄ emission ratio is smaller than that for the Palmerton site, Table 4.2). This is due to the increasing amounts of SO₂ which are transformed as the receptor-site distance is increased for the near field region. The effects of the direct H₂SO₄ emissions from the site are small except at distances within roughly 10-20 km of the site. The total H₂SO₄ atmospheric concentrations are also much smaller than those for SO₂. The reason is that the lifetime of SO₂ with respect to oxidation is about four days in the summer and nine days in the winter (also, the emission rate for H₂SO₄ is much smaller than that for SO₂, Table 4.2). As a result most of the SO₂ escapes into the far-field region without being oxidized.

The next eight figures, Figure 4.9 through 4.16, give atmospheric concentrations of lead for two zinc mine-mill sites, one in Iron County, Mo., the other in Sussex County, N.J., as well as the two smelter sites discussed previously for two seasons each. The great variation in lead concentrations over the sites is due to the variation in emission rates from the different plants, which vary by a factor of 100. The shapes of the isopleths also vary appreciably from site to site and season to season. This shows the effect of different meteorological conditions on the concentration isopleths.

Figures 4.17 through 4.24 give atmospheric concentration isopleths for cadmium. Essentially the only difference between the cadmium and lead isopleths is in the emission rates. Thus, the lead isopleths multiplied by the ratio of the cadmium to lead emission rates give the cadmium isopleths. The effect of the slight difference in the mass distribution between lead and cadmium (Table 4.2) on the isopleth graphs is expected to be small.

Figures 4.25 through 4.28 give atmospheric concentration isopleths for vinyl chloride emitted from polyvinyl chloride manufacture. The differences between these isopleths and those for SO_2 , Figures 4.1 through 4.4, which is also a gas, reflect differences in the stack parameters (these should effect close-in emissions only), meteorological data, emission rates, and transformation lifetimes in air (two days for vinyl chloride versus four to nine days for SO_2).

4.3.2 Deposition Rates

As noted in Section 4.2, the ISC Gaussian model used here enables one to calculate deposition rates for those pollutants that have a coefficient of reflection from the ground of <1.0 . Such calculations were made here for lead emissions. The results are given in Figures 4.29 through 4.36. As is the case for atmospheric concentrations the curves refer to two seasons each for the Iron Co., Sussex Co., Palmerton, and Corpus Christi sites. The values on the isopleths give the deposition rates in nanograms per square meter per second.

4.4 UNCERTAINTIES

The calculation of concentration and deposition isopleths as presented here is subject to many uncertainties. Besides those inherent in the use of a Gaussian model, further uncertainties are introduced by the approximations involved in treating dry deposition, the lack of treatment of washout by precipitation, terrain-elevation effects, and use of offsite meteorological data, etc. In particular, Dungey et al.²¹ have shown that for sites in complex terrain, use of meteorological data from sites which are more than 25-50 km distant from the site of interest can introduce discrepancies of a factor of from 3 to 4 to an extreme of 20 in the calculated concentrations when compared to calculations which use onsite meteorological data.

Uncertainties also exist in the values of plant parameters used in the calculations. These include pollutant emission factors and the composition of the emissions, both of which are often very crude estimates. Such factors also change greatly when pollution control equipment is installed or upgraded, or when processes are changed. This factor becomes important when one considers that the results of this work should apply to the large zinc/halogen battery industry that is projected to be in operation 20 years in the future.

All estimates of pollutant concentrations around industrial sites projected for operation in the future, however, have associated with them uncertainties inherent in the analysis. The approach taken in this document balances 1) the need for a dispersion analysis that is more realistic than the "center-line of the plume with fixed wind direction" approach of the 1980 HEED for Batteries, and 2) the need for a reasonable limit to the number of factors incorporated into the more realistic approach. We have obtained ranges in emission source terms and in other plant parameters by analyzing two different sites for each industry. These sites differ in plant parameters as well as in meteorological conditions for effluent dispersion. Dispersion isopleth graphs at each site are obtained for each of the four seasons, allowing a high and low season to be analyzed for health effects at each industrial location.

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5. ECOLOGICAL IMPACTS

For commercialization of the zinc/halogen batteries, some expansion of the following industries would be necessary:

- Zinc mining, milling, smelting, and refining
- Chlorine and bromine production
- Hydrochloric acid production
- Zinc chloride and zinc bromide production
- Titanium production
- Graphite production
- Carbon black production
- Polyvinyl chloride production
- Polypropylene production
- Teflon production
- Battery complexing agent production
- Polyester resin production

Also, the establishment of battery manufacturing plants would be required.

Details of the emissions from these industries are given in Sections 2 and 3. The significant emissions from the zinc/chloride and zinc/bromine batteries cycles are given in Tables 2.8 and 3.4, respectively. We have also estimated the percentages of U.S. annual production required to sustain production of 1,000,000 modules of each of these batteries; these values are given in Tables 2.11 and 3.8 for the zinc/chloride and zinc/bromine batteries, respectively. As is evident from these tables, the expansion required to satisfy a production rate of 1,000,000 modules per year would be less than 5% for the following industries: chlorine, hydrochloric acid, carbon black, polyvinyl chloride, polypropylene, teflon, and polyester resin.

It can be safely assumed that up to 5% expansion can be accommodated by the existing industries for these materials and that no new facilities would be needed. Further, if we assume that emission levels from these industries are linearly related to the production levels, then no more than 5% increase in emissions would be expected from these industries. Because of the high variability in ecological effects, it is very unlikely that a 5% increase in emissions would result in any measurable ecological effects.

Among the remaining industries requiring more than 5% of the existing annual production, there are several that are either emission free or will have insignificant emissions. These include zinc chloride (p. 20), zinc bromide (p. 44), bromine (p. 44) battery complexing agent (p. 46) and battery manufacture (pp. 27 and 47).

The industries which would have to expand more than 5% and which might have significant emissions include the zinc, titanium, and synthetic graphite producers. Our discussion of the ecological effects, therefore, is limited to the emissions from these three industries. Table 5.1 shows the sorting of the industries involved.

5.1 ZINC INDUSTRY

The significant emissions from mining, milling and primary production of zinc are lead, arsenic, cadmium and sulfur dioxide in addition to zinc itself. Lead and some copper ores are often associated with zinc; thus, the emission values for zinc mining and milling given in Section 2 are over-estimates because they include some wastes that should be attributed to the mining and milling of lead. The biogeochemistry and ecological impacts of these emission constituents were discussed in detail in earlier documents dealing with near-term storage batteries.^{1,2} During the review of HEED for Batteries--1980, recommendation was made by the review committee that the increased loading of the environment with lead from the battery industries be traced through the food chain and that calculations be made on increased uptake of lead via ingestion of food by man. We have followed this recommendation and the approach we have taken for estimating lead uptake in aquatic and the terrestrial food chains is discussed below. The approach is simplistic in the light of the

Table 5.1. Screening of the Battery-Related Industries on Basis of Expansion and Significance of Emissions for Consideration of Ecological Impacts from Production of 10^6 Modules of Zinc/Chloride or Zinc/Bromine Batteries

Industry	Expansion Less than 5%	Expansion Over 5%	
		Insignificant or No Emission	Possibility of Significant Emissions
Zinc			X
Chlorine	X		
Bromine		X	
Hydrochloric acid	X		
Zinc chloride & bromide		X	
Titanium			X
Synthetic graphite			X
Carbon black	X		
Polyvinylchloride	X		
Polypropylene	X		
Teflon	X		
Battery complexing agent		X	
Polyester resin	X		
Battery manufacturing		X	

complex biogeochemistry of lead and should not be assumed to represent a realistic assessment.

As stated in Section 4.1, we have calculated dispersion using pollutant emission rates for actual plant production levels (Zn mine-mills) or for plant capacities (Zn smelter-refiners). A production scenario of 10^6 modules of zinc/chloride and zinc/bromine batteries requires an annual production of 25,000 and 26,000 metric tons of zinc, respectively. The two sites we have chosen for mining and milling assessment are the Buick Mine in Iron County, Missouri, and the Sterling Mine in Sussex County, New Jersey. Each of these sites had annual production of zinc in excess of the amount needed for production of 10^6 modules of zinc/halogen batteries. Similarly, each of the two

smelter sites we have chosen--Palmerton in Pennsylvania and ASARCO in Corpus Christie, Texas--have capacities greater than that necessary to meet the production demands for zinc for 10^6 modules of either of the zinc/halogen batteries. The emission estimates from all these four sites, therefore, are conservative for the assumed scenario of 10^6 battery modules and the impacts attributable to battery production would be less than those estimated in the next two sections.

5.1.1 Lead in Aquatic Ecosystem

Average deposition rate isopleths for lead for the four sites (Missouri, New Jersey, Pennsylvania, and Texas) are given in Figures 4.29 through 4.36. Isopleth at which the Estimated Permissible Concentration for protection of the environment³ (EPC) of $10 \mu\text{g/L}$ of lead will be exceeded by dissolution of this lead in rainwater was calculated for two cases: a) if all deposited lead from the site is dissolved, and b) if only 10% of the deposited lead from the site is dissolved. Isopleth at which lead deposited from the source yields concentration of $10 \mu\text{g/L}$ in annual precipitation runoff has been calculated as follows.

$$R = \frac{10}{P \times F} \quad (1)$$

where

R is deposition rate in $10^{-9} \text{ g/m}^2/\text{sec}$ (from Figs. 4.29-4.36),

P is precipitation concentration factor, based on annual precipitation, as follows:

Missouri Site	283
New Jersey Site	303
Pennsylvania Site	318
Texas Site	364

F is fraction dissolved.

The results are presented in Table 5.2. Emissions from the Missouri site represent the worst case, where, if all lead from this site were to dissolve in average annual precipitation, the lead concentration would be greater than

Table 5.2. Deposition Isopleths at which EPC of 10 $\mu\text{g/L}$ for Lead Will Be Exceeded

Location	Figure Numbers	All Lead Emission from the Site Dissolved in Rainwater	One-Tenth of the Lead Emission from the Site Dissolved in Rainwater
Missouri	4.29 & 4.30	0.035	0.353
New Jersey	4.31 & 4.32	0.033	0.330
Pennsylvania	4.33 & 4.34	0.031	0.314
Texas	4.35 & 4.36	0.027	0.274

10 $\mu\text{g/L}$ and the EPC would be exceeded up to and beyond 100 km from the source. Even if only ten percent of this lead emission were to dissolve, the EPC is expected to be exceeded up to approximately 60 km from the source.

Emissions from the other sites are not as severe as those at the Missouri site. If all deposited lead is dissolved in the rainwater, the EPC of 10 $\mu\text{g/L}$ of lead is exceeded from less than 25 up to about 50 km for the remaining three sites, and if only 10% of the deposited lead is assumed to dissolve, then the EPC will probably not be exceeded except perhaps right at the source.

The mean for lead concentrations in rainwater at 32 U.S. measuring stations has been reported to be 34 $\mu\text{g/L}$.⁴ Supposing that all deposited lead from a site is dissolved in rainwater, this mean value is not exceeded for the New Jersey, Pennsylvania, and Texas sites except right at the source of emission, and this additional lead burden amounts to less than 1 $\mu\text{g/L}$ within 100 km of the source. The Missouri site, of course, is a different story; the isopleth closest to the site suggests a concentration of 1132 $\mu\text{g/L}$, and the level falls to approximately 20 $\mu\text{g/L}$ at 100 km from the source. Comparison of emission values with average rainwater values provides perspective regardless of the EPC values. It would seem that the amount of lead contributed by the battery industries will range from less than 1 $\mu\text{g/L}$ to approximately 15 $\mu\text{g/L}$ for all sites except the Missouri site. We do not consider this to be a cause for

concern. For the Missouri site, however, the additional loading of lead could contribute from approximately 20 to 1200 $\mu\text{g/L}$ within 100 km of the source. Although the toxicity of lead depends on several factors, such high levels have been shown to have acute toxic effects on several fresh water species.⁵ The additive loading of environment with lead with an increase due to battery-related industries therefore, does pose a risk to aquatic biota in the vicinity of the Missouri site, where zinc will be produced in conjunction with mining and milling of lead for the zinc/halogen batteries.

We have reviewed information on the relationship between the amount of lead in fresh water to the amount of lead accumulated in fish. Results reported for Wintergreen Lake, Michigan,⁶ indicate that the amount of lead in fish of various species ranged from as little as 30 to as much as 668 $\mu\text{g/kg}$ for lake water concentrations of 15-20 $\mu\text{g/L}$. The concentration range of 15-20 $\mu\text{g/L}$ in water in this study is very close to that which the additional lead loading of the atmosphere will contribute at the New Jersey, Pennsylvania and Texas sites. As a worst case, therefore, we can assume that the amount of lead in fishes living in the waters in the vicinities of these three locations will be approximately 500 $\mu\text{g/kg}$. Lead is generally not biomagnified and the bioconcentration factors tend to decrease as the trophic level increases. Fish accumulate very little lead in edible tissues, whereas oysters and mussels accumulate high levels. For total aquatic biota the bioconcentration factors are within the range of 10^2 - 10^3 . This is in conformity with the value of 200 to 2500 $\mu\text{g/kg}$ of lead in fish and sea food reported by Schroeder et al.⁷ The range of the natural lead content in food is 10 to 2500 $\mu\text{g/kg}$, depending on the type of food.³³ Considering the value of 500 $\mu\text{g/kg}$ of lead in fish living in water with 15-20 μg of lead per liter and considering that very little of this lead may be accumulated in edible tissues, the additional burden of lead due to battery industries will result in only a small increase in dietary intake as compared to the average daily lead intake. For a better perspective, these values may be compared with the mean lead concentration of 26 $\mu\text{g/L}$ in 29 samples of human milk from USA⁹ and the drinking water standard of 50 $\mu\text{g/L}$ of lead set by the US Public Health Service.¹⁰

We have not found any studies which relate high amounts of lead in water (in the range of 20 to 1200 µg/L expected at the Missouri site) to concentration levels in fish. We, therefore, do not feel confident in projecting the lead levels in fish that may be found at this site.

5.1.2 Lead in Terrestrial Ecosystem

Accumulation of lead in soils can be derived from the simulated deposition rates presented in Figures 4.29 through 4.36. The assumptions behind derivation of soil accumulation rates are presented in Sharma et al.¹ i.e., (1) that all of the deposited effluent is retained in the top 3 cm of soil, and (2) that the bulk density of the soil is 1.5 g/cm³. The deposition rates can be converted as follows:

$$A = 0.7 \times D \quad , \quad (2)$$

where

A is the accumulation rate in µg/g soil per year

D is the deposition rate in ng/m²·sec.

Not all of the lead deposited will be retained by the soil because of physical and biological transport mechanisms. However, it is not possible to make an a priori estimate of the amount of accumulated lead that will be retained in the soil without a detailed knowledge of the lead dynamics in a site-specific situation.¹ Therefore, we have assumed here that the incremental increase in soil lead content due to aerial lead deposition amounts to a year's worth of accumulation. At most of the simulated sites, annual soil lead increments exceed the lead soil EPC (0.02 µg/g) for up to a little over 25 km from the source point (Figs. 4.31-4.36). However, at the Missouri site this EPC is exceeded for a distance of over 100 km from the source point (Figs. 4.29-4.30).

The average lead content of U.S. soils is about 16 µg/g.¹¹ At all sites except the Missouri site, maximum annual accumulation amounts to only about 3% of the national average background levels. At the Missouri site, however, simulated annual maximum accumulation near the source is twice the national

background levels (Fig. 4.29). Indeed, soils in the vicinity of lead smelters have been shown to have lead contents in excess of 100 µg/g for up to 10 km from the source.^{12,13} This is equivalent to 30 to 35 years accumulation of the simulated deposition of lead 10 km from the Missouri smelter (Figs. 4.29-4.30).

The trophic transfer dynamics of lead in terrestrial ecosystems have not been fully studied. Van Hook et al.¹⁴ and Smith and Siccama¹⁵ examined the distribution and cycling of lead in forested ecosystems that were relatively undisturbed. There have been a number of other studies relating soil concentrations of lead to concentrations of lead in plants. Discussions of the concentration ratio of lead in plants vs. soils have reported values ranging from 0.5 to 3.¹⁶⁻¹⁸ The work of Cataldo and Wildung¹⁸ indicates that the concentration ratio can increase with increased available soil lead content. A linear regression of transformed data from the available literature expresses the relationship of soil lead (S) to lead in vegetation (V):

$$\ln V = 0.35 \ln S + 1.4. \quad (3)$$

Regression explains almost 40% of the variation of $\ln V$. The unexplained variation of $\ln V$ is attributable to a variety of factors, including variation among experimental techniques, differences in plant uptake of lead, and differences in soil-lead availability to plants. Thus, this relationship cannot be considered a definitive generalization. Site-specific parameters will have a marked effect upon the concentration ratio of lead in vegetation to lead in soil.¹

Within 10 km of the simulated Missouri smelter, annual accumulation of lead is computed to range from about 3 to 22 µg/g (Figs. 4.29 and 4.30); at the New Jersey smelter annual accumulation within 10 km ranges from 0.04 to 0.2 µg/g (Figs. 4.35 and 4.36). Assuming that background soil levels of lead are 16 µg/g, and a year's deposition accumulated in the soil, soil-lead levels would be raised as high as 38 µg/g leading to an $\ln V$ of 2.6 (from Eq. 3).

Davis et al. found the critical level of plant tissue lead to be 35 µg/g dry tissue for a reduction in barley yield.¹⁹ This value is at the lower end of the range of tissue lead concentrations found to elicit phytotoxic responses.¹

A plant-tissue concentration of 35 $\mu\text{g/g}$ would be equivalent to a soil concentration of about 480 $\mu\text{g/g}$ (from Eq. 3). Although such concentrations have been found within 2 km of active smelters,^{12,13} at the maximum deposition rate of 22 $\mu\text{g/g}$ for the simulated smelter in Missouri (Figs. 4.29 and 4.30), the annual soil accumulation will be less than one-tenth of 480 $\mu\text{g/g}$. Without further site-specific information, we cannot confidently simulate the situation where soil levels could build up to phytotoxic levels due to deposition of lead from smelter operations.

There have been few studies relating the concentration of lead in the tissues of herbivores to concentrations in their food. The review of Hughes et al. indicates that concentration ratios of lead in total body tissue of consumers vs in food range from about 0.1 to 0.8 for herbivorous invertebrates and 0.2 to 1.2 for herbivorous rodents.²⁰ Donn et al. report that cattle's blood levels of lead ($\mu\text{g}/100\text{ ml}$) are related to vegetation ($\mu\text{g/g}$ dry tissue) by a coefficient ranging from 0.05 to 0.7 in a lead smelter region.²¹ Maximum annual lead deposition in the Missouri scenario (Figs. 4.29 and 4.30) could lead to an increase of soil lead to 38 $\mu\text{g/g}$, equivalent to a plant concentration of 14 $\mu\text{g/g}$ dry tissue. Using the highest of the coefficients in Dorn et al. (0.7), blood levels would be about 10 $\mu\text{g Pb}/100\text{ blood}$ in consumers at the simulated smelter. The literature indicates that toxic effects to consumers occur when blood-lead levels approach 50 to 100 $\mu\text{g/ml}$.²²⁻²⁴ Thus, under the highest simulated rates of lead deposition, it is unlikely that toxic levels would build up in consumer tissues if one year-deposition were to accumulate in soils. However, our analysis cannot confidently determine quantitative effects due to several years' accumulation without further site-specific information.

5.2 TITANIUM INDUSTRY

Titanium is used as a heat exchanger in the zinc/chloride battery. It is released to the environment as dust and grindings from machining of the metal and as titanium compounds in sludge and gases from the chlorination and gasification stages in extracting the titanium containing ore. As discussed in Section 2.2.5 (p. 20), since almost all of the titanium ore is imported, no emissions from mining and milling would occur in the U.S. In the chlorination

and purification process, normal operation of the production facilities should not produce any waterborne waste; sludges from the chlorination process produce the only significant solid waste. The sludge contains V, Cr, Zr, Ti, and Cl. Currently these sludges are disposed of by land fill burial or lagoon storage. The airborne emissions would include chlorine, hydrochloric acid, and $TiCl_4$.

Titanium is the eighth most common element in the earth's crust and is present as TiO_2 in rutile and ilmenite ores.²⁵ Ti occurs in nature in the +2, +3, and +4 valance states with TiO_2 as the most common compound. The oxides and hydroxides are poorly soluble and the halides decompose readily in water.³ In the presence of SO_4 ion, the titanium may remain in solution as $Ti_2(SO_4)_3$. The titanic acids (H_2TiO_4 and H_2TiO_3) are insoluble or only very slightly soluble in water.²⁶ $TiCl_4$ in contact with water vapor, soil moisture or groundwater is rapidly oxidized to insoluble TiO_2 or hydrolyzed to titanic acid and precipitates out. In this process, HCl is released.²⁷

Representative natural concentrations of titanium in various components of the biogeochemical cycle are shown in Table 5.3. The concentration is highly variable and ranges from 2-107 $\mu g/L$ in the fresh waters of North America,²⁵ 0.6-1 $\mu g/L$ in sea water,^{25,28} 300-10,000 $\mu g/g$ in soil,^{25,29} and 0.1-0.5 $\mu g/m^3$ in air, increasing from rural to industrial areas.^{30,31}

Toxicity of titanium halides for plant growth has been reported. $TiCl_3$ reduced the yield of bush beans (Phaseolus vulgaris) when present in concentration of 10^{-4} M or greater (approx. 19 ppm). Although most of the titanium remained in the root, 5-10% migrated into the leaves and stem. The plants suffered from chlorosis, necrotic spots on leaves, and stunting.³² On the other hand, titanium sulphate, at a concentration of 10 ppm, had little effect on soil microorganisms but suppression of function in soil microorganisms was observed at 100 ppm.³³ Since titanium halides are unstable, the only places where significant effects on the ecosystem would occur are at sites where constant emissions of toxic amounts occur.

There is very little information on the effects of titanium in aquatic ecosystems. Bacteria growing in a coal ash basin concentrated Ti about eight-fold and in the presence of Cu or Hg the concentration factors in brackish

Table 5.3. Representative Natural Concentrations of Titanium in Various Components of the Biogeochemical Cycle

Component	Concentration
Lithosphere, $\mu\text{g/g}$	400-5700† ¹
Atmosphere, $\mu\text{g/m}^3$	0.01-0.5† ^{1,2}
Hydrosphere	
Seawater, $\mu\text{g/g}$	0.001-0.009† ^{1,2}
Freshwater, $\mu\text{g/g}$	0.002-0.1† ^{1,2}
Pedosphere, $\mu\text{g/g}$	300-10,000† ²
Biosphere	
Marine plants, $\mu\text{g/g}$	12-80† ¹
Marine animals, $\mu\text{g/g}$	0.2-20† ¹
Terrestrial plants, $\mu\text{g/g}$	1.0† ¹
Terrestrial animals, $\mu\text{g/g}$	<0.2† ¹

†¹ Bowen, H.J.M., 1966. "Trace Elements in Biochemistry," Academic Press, N.Y.

†² Berlin, M., and C. Nordman, 1979. "Titanium." In: "Handbook on the Toxicology of Metals," Friberg et al., eds., Elsevier/North-Holland Press.

water were 29- and 11-fold, respectively. In fresh water, the concentration factor was about 1.5 and was not appreciably affected by presence of Cu and Hg.³⁴ The ability of bacteria to concentrate titanium from water may be an entry point for this element into the food chain. We have not been successful, however, in finding useful data on the chemical form and toxicity of titanium compounds that have been combined into organo-metallic complexes and transferred through the food chain. Although titanium halides are known to be toxic, the toxicity of Ti and TiO_2 is very low.²⁷ However, the relatively high bioconcentration factors of aquatic biota (Table 5.4) suggests that the potential for damage to aquatic ecosystems should be further investigated.

Table 5.4. Concentration Ratios for Titanium†¹

Taxon	Habitat	Concentration Factors
Plants	Freshwater	500† ²
Invertebrates	Freshwater	3000† ²
Fish	Freshwater	1000† ²
Plankton	Seawater	20,000† ²

†¹ (Ti) biota/(Ti) medium

†² Braunstein, H.M., et al. 1978. "Environmental and Health Aspects of Disposal of Solid Wastes from Coal Conversion: An Information Assessment." Oak Ridge National Laboratory, Oak Ridge, Tenn.

†³ Braunstein, H.H., C.D. Copenhaver, and H.A. Pfuderer, 1977. "Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview," Oak Ridge National Laboratory, Tenn. Table 9.56, ORNL/EIS-95, E.R.D.A.

Based on current information,^{25,35} most titanium compounds appear to be no threat to health, even under working conditions where exposure levels are high. Although $TiCl_4$ has been recorded as hazardous in industrial accidents, its instability in the environment will present no lasting, widespread damage to the ecosystem or to the human population.

5.3 SYNTHETIC GRAPHITE INDUSTRY

The industrial process for production of graphite is discussed in Section 2.2.6. There are little data in the literature dealing with emissions from graphite production. A recent study indicates that significant amounts of polynuclear aromatics (including benzo(α)pyrene) can be found on analysis of air particulate samples collected during graphite production.³⁶ However, no information is available that would permit us to assess ecological impacts of this industry.

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6. HUMAN HEALTH RISKS

In previous sections, the compositions of the zinc/chloride and zinc/bromine batteries are described, as are the industries required for their production, the emissions associated with these industries, and the dispersion of the emissions into the environment around the major industrial facilities. In this section, the emission information is used to provide an estimate of risk to human health from exposure to emissions constituents.

The first approach (Sec. 6.1) evaluates the effects of environmental exposures utilizing human dose-response functions developed from analysis of the toxicological and epidemiological literature. Dose-response functions for lead and cadmium, presented in the HEED for Batteries, 1980 (ANL/ES-105), are used to analyze the risk to human health of exposure to effluents associated with the production of zinc from zinc ores. These latter two elements are toxicologically important contaminants of zinc ores; these ores constitute the largest single source of cadmium release into the environment. Two new dose-response models are presented; one for exposure to a combination of sulfur oxide and particulates, and one for exposure to vinyl chloride. Sulfur oxide and particulates are emitted during processing of zinc sulfide ores. Vinyl chloride monomer is used in synthesis of the polyvinyl chloride used for battery case construction.

In Section 6.1, we consider the level of general population response to exposures resulting from ground level concentrations in the near-field pollutant field of six locations identified for halogen battery component manufacture. The near-field is defined as a rectangular surface 180 km on a side which surrounds the manufacturing site. The sites chosen are identified in Section 4 of the present report. Dispersion plots presented in Section 4 for source-specific emissions were generated by season. For a given industrial site, two plots, one with maximum and one with minimum ground-level concentrations are selected for evaluation. The two seasonal plots representing the concentration extremes from each site are then used to estimate incremental health risks

over and above those associated with the natural background concentrations existing at each site. Health effects are analyzed for effluents from whole industrial sites, as presented in Section 4 isopleth graphs, and thus are not tied to a given scenario for battery production. It can be noted that a scenario requiring production of 1×10^6 battery modules per year would require the following percentages of the output from one industrial site: ~75 percent of production levels for the zinc mine-mill complexes analyzed; ~25 percent of plant capacities for the zinc smelter-refiners analyzed; 35 percent (for zinc/chloride battery) or 2 percent (for zinc/bromine battery) of plant capacities for the polyvinyl chloride manufacturing sites analyzed.

The estimate of risk for each agent is presented in terms of numbers of individuals anticipated to be adversely affected by continuous exposure to the ground level concentrations of the identified agent. The exposure is assumed to continue for at least one year. Further, the exposure is assumed to be constant for points within the pollutant field between two consecutive isoconcentration lines. In order to present an overall level of population risk, surface areas between isoconcentration lines, impinged by each ground-level concentration, were estimated. Surface areas were then identified with their geographical analogues, and county-level population density factors were used to calculate populations of each area. With the three risk components (risk factor, surface area of concern, population density), it was possible to generate an approximate number of persons at risk of being adversely affected by the total pollutant field (32,400 km²).

Section 6.2 examines health and safety effects among the occupationally exposed through (1) application of the dose-response models to possible workplace exposures, where appropriate, and (2) analysis of data on rates of occupational injury. In the occupational injury section, as in the environmental exposures section, an attempt is made to estimate total numbers of persons at risk from occupational injury, in addition to presenting data on injury incidence rates.

Section 6.3 presents an analysis of anticipated health effects from chlorine exposures as a result of chlorine release under various accident scenarios involving electric vehicles powered by zinc/chlorine batteries. The

effects of exposure to titanium and graphite are also briefly described. These additional components of the zinc/halogen battery systems are ones for which human dose-response information is not available.

6.1 ENVIRONMENTAL EXPOSURES

The analysis of health risk for the zinc/halogen battery attempts the quantification of the level of general population risk anticipated from a continuous emission of four agents identified in various intermediate process streams of the zinc/halogen battery industry. The agents selected for evaluation are airborne respirable particulates of lead, cadmium, polyvinyl chloride (as monomer) and a combined emission of sulfur oxide with particulates. Models for assessing risks from lead and cadmium were presented in the previous year's battery HEED (ANL/ES-105). These models are used in the present analysis, with minor updating resulting from additional information obtained during the year since publication of the previous document.

The risk model for vinyl chloride exposure and induction of angiosarcoma of the liver is new to this year's HEED and is presented in detail in the risk section of the present document. The sulfur oxide-particulate model is based upon an early version of the Lave and Seskin (L&S) sulfate model for estimating total mortality. The sulfate analysis, unlike the previous agent models, is a direct calculation of general population mortality. It therefore takes an analytical form that allows its inclusion into a model that recognizes the dynamic nature of population structure, competing risks, and latency of response. For the present analysis, the L&S model is therefore appended to a population projection model developed at Argonne National Laboratory. The results of this model are believed to be reasonable estimates of the level of general health risk, whereas estimates from the previous models are more correctly interpreted in terms of a specific or unique health risk end point, a single effect. This point is noted primarily to justify the apparent disparity between the level of calculated response for the L&S model and those for the other three agent-specific models in this report.

6.1.1 Sulfur Oxides and Particulates

A Demographic Model to Estimate General Population Response to Atmospheric Sulfur Oxides and Particulates

The core of any risk assessment scheme is the exposure-response model. This is a quantitative relationship between the level of exposure to the hazard and the deleterious effects to the population. In general, the chance of observing the effects of a given hazard depend on the level of exposure, the duration of exposure, the duration since the onset of exposure and the intensity of competing risks from other causes of mortality. This suggests that a health risk projection should not only include a dose-response function but also should model the population structure, latency of response and competing risks from other causes of mortality. In addition, the model should provide both aggregate mortality levels and individual risk so as to be most useful to the policy maker. Finally, a health risk projection should be able to realistically follow populations through time.

The present model incorporates age, fertility, and mortality structure to follow populations through time under a specified pollution exposure regime. The model incorporates age-specific dose-response data together with a Leslie projection matrix projection technique to produce a simulation of a continuous population exposure response. In addition to expected values, confidence intervals are calculated for the projection model using a Monte Carlo approach.

Three characteristics of a population exposed to environmental pollution make the use of this type of model necessary for obtaining realistic estimates of health impacts. First, the risk of developing chronic disease appears to follow age-specific patterning. Second competing risks from other causes of mortality reduce excess deaths from pollution exposure. This is especially important in diseases with long latency between exposure and onset of disease. Finally, it is important to consider fertility levels and age structure so that births occurring during exposure can be taken into account since the birth level will determine the size of the future population that will be exposed.

The utility of employing this model is demonstrated by a relative risk, nonthreshold formulation. In this type of model, age-specific response coefficients are multiplied by population exposures integrated over a time interval to determine the excess number of deaths, where the relative risk, nonthreshold formulation defines a proportional increase in risk of death over the underlying rate, which varies linearly with respect to dose, so that:

$$\mu(x) = \mu'(x) \sum_{i=x_0}^x r(i)h(i)B(i,x) ,$$

where

$\mu'(x)$ = the underlying risk of death (in deaths per person-year)

$\mu(x)$ = excess risk associated with exposure

$r(i)$ = level of exposure at age i (in ppm)

$h(i)$ = latency multiplier for duration $i - x_0$ since exposure

= 1 if $i - x_0$ is greater than the period of latency and less than the sum of the period of latency and the plateau period,
= 0 otherwise.

$B(i,x)$ = response coefficient relating the proportional increase in $\mu(x)$ to exposure accumulated at age i .

The demographic model approach to health risk projection does a complete dynamic simulation of the fully structured population at risk as well as the dose-response function. The population at risk is simulated by using the standard component projection technique. This technique generates cross-sectional estimates of the age, sex structure and population size. This technique is outlined briefly for single-year projections as follows:

- 1) Compute the age-specific deaths, m_x , at age x as

$$m_x = \frac{D_x}{P_x} ,$$

where D is deaths and P is the population.

- 2) Convert these rates to probabilities, q_x

$$q_x = \frac{2m_x}{1 + 1/2 m_x} .$$

- 3) Calculate sequentially the number in the hypothetical cohorts surviving from birth to exact age x as

$$\ell_x = \ell_{x-1}(1 - q_x) .$$

- 4) Estimate person-years lived in the x interval

$$L_x = \int_0^1 \ell(x + t) dt .$$

- 5) Calculate survivorship rates

$$S_x = \frac{L_{x+1}}{L_x} .$$

- 6) These survivorship rates, along with the relevant fertility information, are used to construct the Leslie matrix. This matrix is then used to multiply a population vector at time t to estimate a population vector at time $t + 1$, or

$$\begin{bmatrix} P_{t+1} \end{bmatrix} = \begin{bmatrix} L \end{bmatrix} \cdot \begin{bmatrix} P_t \end{bmatrix} .$$

This component method of a population projection can be easily turned into a health risk projection model in the following way:

- 1) Assuming independence of the cause of death, compute the excess mortality rate for a relative risk model as

$$m'_{ijk} = R \cdot E \cdot m_{ijk} ,$$

where:

m_{ijk} = baseline mortality rate at each age i , sex j , and disease k

m'_{ijk} = excess mortality rate at age i , sex j and disease k

R = slope of dose-response function

E = exposure level

- 2) Then the total age-, sex-, disease-specific mortality rate, m''_{ijk} , in the presence of an effluent is

$$m''_{ijk} = m'_{ijk} + m_{ijk}$$

- 3) Summing the mortality rates by cause, we then calculate a life table and construct modified Leslie matrix to estimate a future population structure in the presence of an effluent, or

$$\begin{bmatrix} P_{t+1} \end{bmatrix} = \begin{bmatrix} L' \end{bmatrix} \cdot \begin{bmatrix} P_t \end{bmatrix}$$

- 4) This process is repeated until the desired end point has been reached.

The resultant outputs from this type of modeling approach includes a number of summary statistical measures referring to population health response and individual health risk from exposure to agents that influence health status. Measures of particular interest to issues of environmental policy include probability of dying from a specific cause of death such as cancer, life expectancy at age 0, as well as the age-standardized death rate for a specific disease or condition. An overall level of population response can then be determined from these measures.

The health-risk projection model used in the present analysis was developed at Argonne National Laboratory for the express purpose of estimating incremental risk levels associated with minor elevations in both radiological and non-radiological air pollutants. The preceding discussion is abstracted from material published in journals concerning the theory and operation of the ANL model.^{1,2} This model includes arguments of dynamic population structure in terms of age structure, mortality, and fertility effects, competing mortality risks from various diseases, and latency of chronic disease. As such it is believed to present a reasonable estimate of the level of population health impact, as excess deaths per year, along with individual level of risk, as decreased expectation of life (E_0), that can be expected to occur under conditions of long continuous exposure of the population under a specified exposure regime.

The Lave and Seskin Model of Population Mortality Response from Air Pollution

In the present analysis we are concerned with the potential health impact of sulfur oxide and particulates emitted in the airborne emission streams associated with the operation of electric battery technology. Perhaps the best-documented health effects model for these agents is the one developed by Lave and Seskin.^{3,4} This model specifies an age-specific mortality response for long-term exposure to air pollution and is briefly described in the following statement. The age-specific coefficients derived in the Lave and Seskin model form the basis of the dose-response module of the population risk projection model previously described in this discussion.

The health effects of long-term exposure to low concentrations of air pollutants are hypothesized to be subtle. Thus, laboratory methods are of little help in estimating the dose-response curve, even though they may be powerful in exploring the underlying physiological mechanisms. Epidemiological methods are concluded to be the most reasonable ways of examining this association.

Data from three years, 1960, 1961 and 1969, for 100 U.S. SMSA's (standard metropolitan statistical areas) were used to evaluate the association between specific measures of air pollution and mortality. The measures of air pollution, sulfates and suspended particulates, were found to be among the significant factors explaining variation in the total death rate across areas of the U.S. Air pollution was also a significant factor in explaining the variation in the age-sex-race specific rates. It was estimated from these results that a 50% reduction in ambient levels of sulfates and suspended particulates was associated with approximately a 0.8-year increase in life expectancy at birth.

Examination of disease-specific mortality rates using 1960 and 1961 data revealed a close association between air pollution and total cancer deaths. Deaths from cardiovascular disease also showed a close association with sulfate pollution. It was concluded that the results of the disease specific analysis support the general assumption that measures of air pollution are significantly associated with mortality, even after the rates were disaggregated by disease and adjusted by age, sex and race.

The proposed form of the Lave and Seskin model is:

$$Y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \mu,$$

where Y is the mortality rate, X_1 is the cumulative exposure of air pollution that the population has experienced, X_2 is a socioeconomic index and μ is an error term, while α_0 , α_1 , and α_2 are coefficients to be estimated. This model incorporates two restrictive assumptions. The first is that populations are assumed to be nonmigratory and the second is that pollution levels have remained constant at the same relative levels over time.

Lave and Seskin conclude from their analyses that the statistical evidence, in conjunction with knowledge gained from epidemiological studies of particular groups, laboratory experiment, physiology, and air chemistry are consistent with the conclusion that a causal relationship has been demonstrated for air pollution exposure and population mortality response. In the present analysis it was assumed that the pollution health effect was a chronic response due to long-term exposure, and further that the population effect was more a late life rather than a continuous threat. Therefore, the predominant response would be from members of the older population age group.

Six pollution variables representing sulfur oxide and particulate air pollution measures were evaluated by Lave and Seskin. The two variables found to have the greatest significance in the mortality association were minimum biweekly sulfate and annual arithmetic mean total suspended particulate concentration. These two variables were found to explain 83 percent of the variation in the mortality association. An increase of $1 \mu\text{g}/\text{m}^3$ in sulfate was related to an increase of 4.7×10^{-5} in the total death rate and an increase of $10 \mu\text{g}/\text{m}^3$ of TSP was related to an increase of 3.0×10^{-5} in the total mortality rate.

Rationale for the Choice of a Specific Health Risk Model for General Population Response to Airborne Sulfur Oxides and Particulates.

In the present analysis it is deemed inappropriate to discuss the various arguments presented in the literature concerning the presence or absence of

air pollution health effects. The subject has been treated extensively, and many well-documented discussions on the subject are available. The interested reader is referred to the article by Ferris⁵ in the Journal of Air Pollution in which the author discusses the data base supporting adverse health findings for the criteria pollutants. A later discussion of this paper by Drs. Higgins, Waller, Chapman and Goldsmith was published in the same journal.⁶ Extrapolation of health effects is covered in chapter six of the book by Wilson⁷ on the health effects of fossil fuel burning.

In the present discussion we start with the assumption that a general population response to low-level concentrations of sulfur oxides and particulates may exist. An additional assumption in this regard is that the model proposed by Lave and Seskin is a reasonable representation of an air pollution effect. This latter assumption is supported by information presented in Wilson's book, wherein the mortality response coefficients for sulfur oxides and particulates are compared in a number of different studies. Although the results of this comparison are anything but consistent, the Lave and Seskin model coefficients are, at the least, consistent in sign and order of magnitude with the majority of the other studies considered.

Thibodeau et al.⁸ also critically reviewed the Lave and Seskin model and concluded also that although the authors have reservations concerning the "best fit" for an air pollution model they do not disagree with the general conclusion of the existence of the association as presented by Lave and Seskin.

In an analysis of risk, therefore, it would seem prudent to assume that a health response does in fact exist and that, for the sake of argument, the Lave and Seskin model is a reasonable representation of the overall general population health risks associated with long-term exposure to airborne sulfur oxides and particulates. The final conclusion as to the existence of an air pollution health effect has yet to be determined. In all likelihood such a determination is many years distant and without doubt beyond the time schedule of the present assessment.

Analysis of the Health Risk Posed by Exposure to Point Sources of Sulfur Oxides and Particulates

Two sites associated with the zinc/halogen battery industry were selected for an analysis of sulfur oxide/particulate health risk. These sites, Palmerton, Pennsylvania, and Corpus Christi, Texas, were identified in the technology description section of this report as important sources of sulfur oxide and particulate emissions resulting from the manufacture of zinc/halogen batteries.

The level of health risk for populations living within 90 km of the point sources were analyzed by means of a population mortality projection model developed at Argonne National Laboratory. Results are reported for male and female populations in terms of absolute number of deaths which can be directly attributed to the effect of air pollution on exposed populations in excess of general base-line mortality. In addition to number of deaths, a separate parameter, expectation of life, was calculated for persons under defined maximal exposure conditions. Expectation of life identifies the level of individual risk by representing a fractional decrease in personal lifetime from that of the average population excluded from a given exposure regime. The exposure regime definitions utilized an assumption of continuous TSP exposure at a seasonal maximum value, upon which a seasonal sulfur oxide exposure was modulated and an SO₂ to sulfate conversion rate was applied.

The results of the risk analysis are presented in Table 6.1 and Figure 6.1. The Pennsylvania site is shown to have the highest relative risk when compared to that of the Texas site. The seemingly large impact calculated for the Pennsylvania site should be interpreted not so much in absolute number of deaths but rather as many small life-shortening events. The results of this analysis are presented in terms of annual level of impact. The analytical projection itself was conducted for a 25-year period. Therefore, the annual risk levels can be interpreted as average impact levels anticipated over the continuous operation of a zinc/halogen battery manufacturing industry. Because of the nature of the assumed population exposure, a dynamic population structure followed for 25 years, and the inclusion of competing causes of death in the projection model, it is believed that the health impact presented is a reasonable estimate of the level of general population risk anticipated as a result of

Table 6.1. Health Risk from Exposure to Airborne Sulfur Oxides and Particulates

Site	Air Concentrations above the Primary Air Quality Standard (AQS) ^{†1}		Total Exposed Population	Annual Level of Risk ^{†2}		
	Ranges of SO ₂ Concentrations (µg/m ³) (Annual Avg.)	Total Suspended Particulate Concs. (µg/m ³) (Annual Avg.)		Estimated Number of Deaths ^{†3} (annualized)	Expectation of Life (E ₀) ^{†4} (years)	
Palmerton, PA	0.03-0.8 ^H	5.4 ^H	12,765,000	Male	10.7-31.9	68.1-68.4
	0.01-0.6 ^L	1.8 ^L		Female	5.9-17.4	76.3-75.8
Corpus Christi, TX	0.01-2.0 ^H	1.5 ^H	994,000	Male	0.6-0.9	68.4-68.4
	0.01-1.25 ^L	0.9 ^L		Female	0.3-0.5	76.2-76.3
Baseline (exposure assumed to be at primary AQS)	0(80) ^{†5}	0(75) ^{†5}	213,000,000	Male	(9660) ^{†6}	68.6 ^{†6}
				Female	(8550) ^{†6}	76.6 ^{†6}

^{†1} H = seasonal high, and refers to summer season concentrations at Palmerton, PA and winter season concentrations at Corpus Christi, TX. (To bound the analysis, seasonal values are assumed equivalent to annual average concentrations).

L = seasonal low, and refers to winter season concentrations at Palmerton, PA and to summer season concentrations at Corpus Christi, TX.

Concentrations of SO₂, and derived sulfate concentrations, are presented as isopleth graphs in Section 4. For a given season and industrial site, a single TSP concentration was used.

^{†2} The response range presented represents seasonal variation in exposure levels. Responses given are those for seasonal high and seasonal low exposure regimes.

^{†3} Mortality experience of the population attributable to the effects of airborne sulfur oxide and particulates. For comparison, deaths attributable to the effects of air pollution in the total U.S. population are presented in parentheses as a baseline case.

^{†4} E₀ is expectation of life in years, and is a measure of individual risk. Expectation of life for exposed populations should be compared to values shown for the baseline population.

^{†5} Concentrations in parentheses are primary AQS concentrations.

^{†6} Range estimates for these mortality and expectation of life values, derived from statistical variation in E₀ at the level of county size populations throughout the U.S., are 8930-10400 and 63.4-73.8 for males, and 7890-9210 and 70.7-82.5 for females.

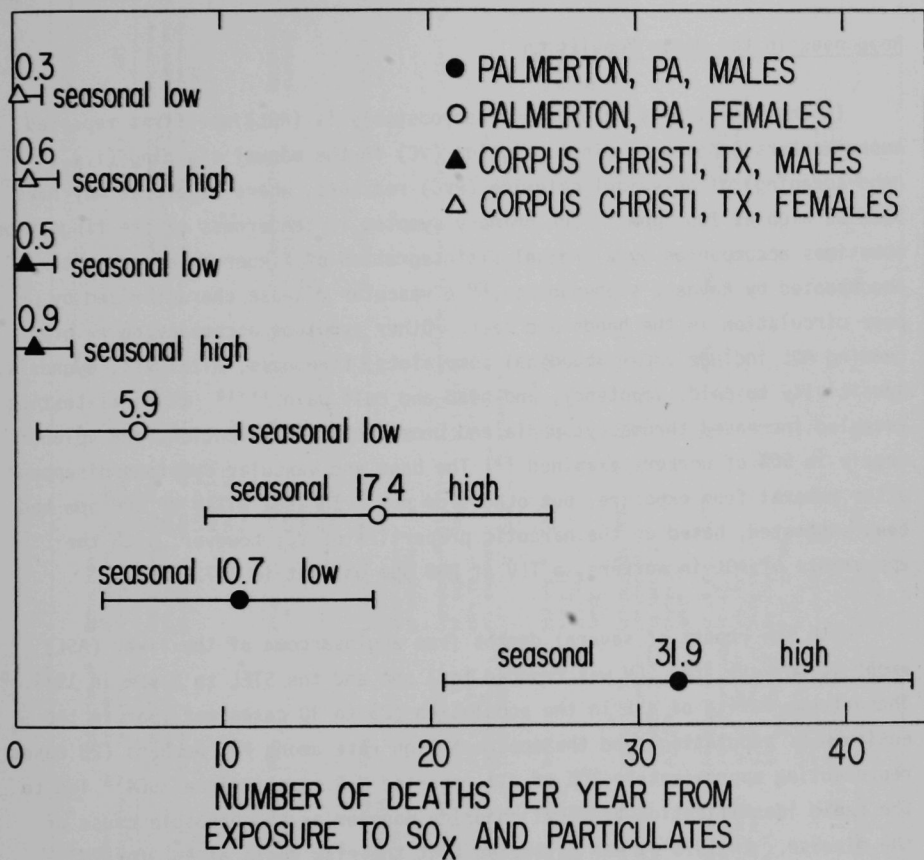


Figure 6.1. Ranges in Estimates of Deaths per Year from SO_x and Particulates for All Industrial Sites Analyzed.
Effects of (1) uncertainty in each risk estimate (mean $\pm 2\sigma$, where $|\sigma| = \sqrt{\text{mean}}$), (2) differences between sexes, and (3) differences between industrial sites are presented.

long-term continuous exposure to sulfur oxides and particulates emitted during battery manufacture.

6.1.2 Vinyl Chloride

Responses in the Human Population

In the late 1960's occupational acroosteolysis (AOL) was first reported among workers exposed to vinyl chloride (VC) in the manual cleaning (i.e., hand scraping) of polyvinyl chloride (PVC) reactors, where exposures may have been as high as 1000 ppm.⁹ The primary symptom is tenderness of the fingertips sometimes accompanied by a gradual disintegration of finger bones and often accompanied by Raynaud's phenomenon,¹⁰ a vascular disease characterized by poor circulation in the hands and feet. Other symptoms accompanying or preceding AOL include upper abdominal complaints, tiredness, dizziness, cyanosis, sensitivity to cold, impotency, and head and calf pain.^{11,12} Clinical testing revealed increased thrombocytopenia and bromsulphalein retention, and splenomegaly in 50% of workers examined.¹¹ The bone and vascular symptoms disappear after removal from exposure, but others do not. In 1961 a TLV of 500 ppm had been suggested, based on the narcotic properties of VC; however, with the appearance of AOL in workers, a TLV of 200 ppm was set in 1972.

With the report of several deaths from angiosarcoma of the liver (ASL) among VC workers, the TLV was reduced to 1 ppm and the STEL to 5 ppm in 1974.¹⁰ The extreme rarity of ASL in the population (25 to 30 cases per year in the entire U.S. population) and the apparent high rate among PVC workers (23 cases representing approximately 10% of all reported U.S. cases since 1964¹³ led to the rapid identification of vinyl chloride monomer as the probable cause of the disease. In 1975 it was estimated that the risk ratio of ASL for PVC workers is approximately 400:1.¹⁴ The general public may also be at risk from indirect exposure by residing near VC fabrication of polymerization plants. Brady and coworkers¹⁵ found 19% of New York State ASL victims lived closer to such plants than did their age-, sex-, race-, residence county-matched controls.

There are no clinical tests or symptoms specific to angiosarcoma of the liver. In general, its victims suffer "fatigue, abdominal pain, weight loss,

Table 6.2. Occupational Cohort VC Studies

Study	Cohort Size	Cohort Qualification	Estimation of Exposure Intensity	Estimation of Exposure Duration	Follow-Up of Cohort	Total Deaths	Increased Risk of Cancer				
							Angiosarcoma of Liver	Other Liver and Biliary	Lung	CNS	Lymphatic and Hematopoietic
Tabershaw & Gaffey, 1974 ²⁴	8384 employees in 33 plants	At least 1 yr. of exposure prior to 12/31/72	Estimated by industry personnel	Compared <5 yrs. with >5 yrs.	85% followed; death certificates for 93% of those followed	352	Yes-6	Not considered separately	Insignificant increase in SMR	Insignificant increase in SMR	1 each, SMR insignificant
Monson, Peters, & Johnson 1974 ³⁶	Total employees unknown, 2 plants	Death between 1947-1973	None	None	100% of active or retired workers who died	161	Yes-5	Yes, but due to angiosarcoma	Yes	Brain, 4x expected	Yes, 50%
Nicholson, et al., 1975 ⁹	257	5+ years exposure between 1947-1963	None	Latency of 10 years after onset of exposure	99% followed	24	Yes-3	No deaths	No deaths	Brain-1	2 Deaths
Ott, Langner, & Holder 1975 ²⁵	594 employed 1942-1960; 72 exposed to arsenicals	All employees between 1942-1960 with potential exposure	Air sampling; estimates by job classification <25, 25-200, 200+ ppm	Compared <1 yr. exposure to >1 yr. exposure	91% followed	89; 10 of those exposed to arsenicals	No deaths	No deaths	Yes-5	Brain-1	1 Leukemia also exposed to benzene
Maxweiler et al., 1975 ²⁵	1294 employees, 4 plants	5+ yrs. exposure, 10+ yrs. since onset of exposure	None	≥10 yrs. and > 15 yrs. latency	99.5%	136	Yes-11	Yes	Yes	Brain 9 glioblastoma multiforma	Yes
Fox & Collier, 1977 ²⁷	7717 employees, Great Britain	employed between 1940-1974	estimated by industry personnel 200+, 25-200 <25 ppm	Latency not considered in specific causes of death	99%	409	Yes-2	Yes-2	No	Yes	No
Buffler et al., 1979 ²⁸	464 employees, 1 plant	2 consecutive months exposure between 8-1-48 and 9-25-75	Estimated from 1971 air samples by job classification; index of $\frac{\text{time} \times \text{exposure}}{\text{time}}$ compare those above vs. below mean	<2.29 yrs. vs. >2.29 yrs. for those who survived a 5 yr. period ending 9-25-70	100%	28	None	None	Yes, 1 also exposed to 1, 4-dioxane		
Byrén et al., 1976 ¹⁸	771 employees, Sweden	All employees	Estimated by industry personnel	<5, 5-9, ≥10 yrs.	97%	58	Yes	Yes	No	Yes-brain	No deaths reported

anorexia, nausea, vomiting, melena, indigestion, jaundice, hematemesis or diarrhea.¹⁶ After a latency of 13 to 20 years,¹⁷ the disease suddenly becomes apparent and progresses rapidly to death within 1 to 16 months.^{16,18}

Some occupational studies (Table 6.2) have reported cancer at other sites. These include brain cancer (glioblastoma multiforme) and, with less certainty, lung cancer. Other, noncarcinogenic effects among workers were reduced air flow and volume,¹⁹ increased chromosome aberrations,²⁰ portal hypertension, deafness, blindness, immune complex disorders, nervous system disorders²¹ and increased fetal wastage in wives of male workers.^{22,23} Community studies centering on reproductive characteristics^{22,24} are suggestive, but in no way definitive, as to the possible general population effects of PVC manufacture.

The general public is currently exposed via contaminated air, water, or food. Air emissions from VC and PVC plants are said to account for 96% of atmospheric emissions. Incineration of plastics also contributes to air levels of VC. Although higher levels may periodically occur, over 90% of the time they are below 1 ppm in the vicinity of VC and PVC plants. The EPA estimates the general population average is 0.5 ppb, and about 0.017 ppm for the 4.6 million people living within five miles of VC plants. Food can contribute an additional 1 µg/day as a world average; however, data are inadequate at present to determine a dietary intake for Americans. Current occupational exposures range from < 1 ppm up to 10 ppm in PVC plants, 0.07 to 26 ppm in VC monomer plants, and 0.01 to 2.4 ppm in fabrication plants, with the majority of the latter averaging less than 0.01 ppm.¹⁰

A Model to Estimate General Population Response

Despite numerous occupational cohort studies of vinyl chloride exposure (Table 6.2) dose/response information is still scant. Several studies^{14,25,26} indicate an increasing risk of angiosarcoma of the liver with time since initial exposure. An increasing risk of liver cancer (largely due to ASL) is also associated with increasing levels of exposure.^{26,27} In the former study, the SMR for liver cancer was 1539 at the highest exposure level (> 200 ppm) and 132 for less than 200 ppm exposure. The data of these authors and those

of Heath et al.¹⁴ indicated a dose relationship in that those persons experiencing higher exposure levels had shorter latencies. Unfortunately, no two of the studies in Table 6.2 are comparable; exposure estimates tend to be crude. In a study with some of the better air sampling data²⁸ no deaths from ASL were reported. In the latter case, as in so many others, exposure levels were retrospectively determined by persons familiar with the industrial process. Only in very recent years (post-1970) has air sampling actually been conducted, and the time period since its inception is much too short to determine a cancer risk with a 13-20 year latency period. An additional problem with exposure estimates is that workers tend to enter the industry at the lowest job classifications and highest exposure levels.²⁹ After varying amounts of time they advance to higher job categories and lower exposure levels. Thus the occupational studies provide only an indication of dose/response, but are insufficient for derivation of a possible model.

Lacking sufficient human data to derive a dose-response model, it was necessary to turn to animal data. Gehring and coworkers^{30,31} have developed an animal-based model, using the experimental exposure-response data of Maltoni and Lafemine³² and their own data on vinyl chloride metabolism in rats. Their model simply states that it is a biotransformation product of VC which is carcinogenic, and dose in humans can be estimated from rats by adjustment for metabolic, body mass, and body surface area differences. Further, the biotransformation process is assumed to follow Michaelis-Menten kinetics, and a probit model best agrees with angiosarcoma incidence from epidemiologic studies.

Anderson and coworkers³³ have criticized the Gehring et al.³¹ model for incomplete comparison of mathematical models and pointed out the importance of an accurately calculated duration of exposure, which if not carefully done can underestimate the lifetime human risk. The former proposed their own model incorporating pharmacokinetics to arrive at a low-dose estimation which may better reflect reality. Although these arguments are suggestive of alternative interpretations of the Gehring et al. model, they do not nullify the use of the model in risk estimation, particularly considering the sparse data base.

The Gehring model can be considered conservative. By the authors' own admission, it overpredicts human ASL incidence at low doses compared to death

rates available from occupational studies. We found that it also underestimates incidence for ASL in rats at high exposures (250+ ppm) compared to the experimental data of Lee et al.³⁴ and Radike et al.³⁵ However, the latter predictions differed from the actual rates by only 2- to 3-fold, which is acceptable for our purposes. Thus, the model is at best a first order estimate.

In the first of two papers Gehring and coworkers³⁰ showed that inhaled VC is biotransformed in rats in a nonlinear process following Michaelis-Menten kinetics:

$$v = V_m S / (K_m + S) \quad , \quad (1)$$

where

v = velocity of transformation in $\mu\text{g/hr}$,

V_m = maximum velocity of transformation in $\mu\text{g/hr}$,

K_m = Michaelis constant in $\mu\text{g VC/liter air}$,

S = concentration of VC inhaled in $\mu\text{g/L}$ (1 ppm = 2.56 $\mu\text{g/L}$)

For a human exposed 8 hours per day, equation (1) adjusted for human metabolism and physiology is:

$$v \mu\text{g}/8 \text{ hr} = \frac{1675 \mu\text{g/hr} \cdot S \mu\text{g/L}}{860 \mu\text{g/L} + S \mu\text{g/L}} \quad (2)$$

In the second paper,³¹ it was shown that a probit equation best describes the total ASL rate, as seen in a recent epidemiological study of VC workers. A working life of 35 years was apparently chosen because it improved the fit of the model to the observed data.

From the inhaled dose a probit percent incidence can be derived:

$$\text{probit } \% = -1.625 + 1.543 \log v \quad (3)$$

The coefficients for equation (3) were derived from data on rats.³⁰ Finally, the probit can be converted to an incidence rate. This step was not fully described by the authors, but from information in Table 3 of Gehring et al.,³⁰) this relationship was found to be:

$$\% \text{ incidence} \times 10^{-6} = 2.288 \times 10^{-5} e^{4.15X} \quad (4)$$

where x = probit %, and the correlation coefficient is 0.99.

Gehring et al.³¹ predicted that a 35-year exposure to 1 ppm VC for 8 hr/day, 5 days/week would result in 1.5/100,000,000 angiosarcomas of the liver among workmen so exposed. Using equation (4), we arrive at a predicted incidence which is slightly higher, 2.3/100,000,000, but certainly acceptable given data available.

The model presented appears to be almost equally sensitive to the values of V_m and S in equation (2) and less sensitive to the value of K_m . Therefore, major uncertainties are the accurate extrapolation of rat data to humans and determination of VC exposure levels.

Analysis of Human Response to Emissions from Battery-Related Industries

Seasonal vinyl chloride concentrations, within the areas around the two sites for polyvinyl chloride manufacture analyzed in Section 4, range from a set of low isopleth concentrations during the spring at the Maryland site, to a set of high isopleth concentrations during the fall at the Oklahoma site. The highest general population exposure to PVC is likely to occur during the fall at the Oklahoma site. The maximum vinyl chloride concentration achieved at the latter site was $26.7 \mu\text{g}/\text{m}^3$. (This maximum concentration was computed by the program used for VC dispersion analysis, but does not appear on any of the isopleth lines). The model predicts that this exposure level, $26.7 \mu\text{g}/\text{m}^3$ or $0.0267 \text{ mg}/\text{L}$, could result in an ASL incidence of $0.001 \times 10^{-6}\%$, or $1/10^{11}$,

for a 24-hr/day, 7 days/week,* and a 25-year exposure period. Not only is this incidence rate insignificant, it is also an overprediction of unknown magnitude. However, it can be said that, in comparison, an exposure level nearly 100-fold greater gave a 50-fold overprediction of occupational exposure and ASL incidence.³¹ Since the highest expected exposure level resulted in a prediction of an insignificant ASL incidence, further examination of the predicted PVC general population exposure levels was deemed unnecessary.

6.1.3 Lead

The model used in the present analysis to assess population health impact from airborne particulate lead was that presented in the HEED for 1980 (ANL/ES-105). The model described in the 1980 HEED proposes a continuous relationship between long-term exposure to airborne particulate lead and an incremental rise in health risk as defined by the probability that an individual will exhibit a continuous blood-lead level in excess of 60 µg/ 100 ml of whole blood. Such a definition is consistent with a minor increase in the likelihood that any given individual in a group of persons, continuously exposed to constant concentrations of airborne lead for periods of time approximating one year in duration, will display overt signs of lead intoxication, as defined by hematopoietic (anemia) and/or nervous system disfunction responses. The model is conservative in that likelihood of a blood lead in excess of the defined hazardous level is inferred from an assumed continuous probability function based on the average population blood-lead level.

One modification has been made in the present year's model. The population blood lead level variation was redefined based on additional information. The new variability definition is taken from the published works of Pueschel,³⁷ Vitale,³⁸ and Lagesson.³⁹ The data presented in those studies define a range of observed blood lead levels in different populations. This redefinition of

*The original model assumed 8 hr/day, 5 days/week and 35-years. The value of S (equation (1)) can be directly adjusted for 24 hours. The number of exposure days per week must be indirectly adjusted by using 5/7 of the 35-year exposure period, or 25 years' exposure.

the variation inherent in the blood-lead measure leads to a risk estimate that is substantially below the more conservative assumption of a log linearity for variation.

The following table describes the quarterly ground-level exposure conditions selected for definition of an exposure range.

	<u>Maximum</u>	<u>Minimum</u>
Missouri	Winter	Summer
Texas	Winter	Spring
Pennsylvania	Fall	Winter
New Jersey	Winter	Summer

Table 6.3 presents estimates of the level of health risk anticipated from lead emissions related to various aspects of zinc/halogen battery manufacture. The units in this table represent the number of persons per year expected to have elevated blood lead concentrations indicative of lead intoxication. Since the model used assumes an incremental effect dependent upon ambient exposure levels, a background level of response is also included with the estimate of total response. The differential level, labeled increment, therefore represents the actual numbers of elevated blood leads attributable to the point source emission. An additional measure, normalized response, is the overall level of individual risk of adverse blood lead response that can be compared between industrial sites. As would be anticipated, the site with the greatest point source, Missouri, has the largest health impact measured in terms of both total individuals responding and individual risk. Locations associated with relatively small point source emissions yet in high population density areas (Eastern Pennsylvania, Northern New Jersey), have a minimal level of risk.

6.1.4 Cadmium

The cadmium model developed in the HEED for 1980 (ANL/ES-105) for risk analysis relates daily air exposure to a kidney concentration and subsequently to an average urinary protein level. The actual level of excess risk is found

Table 6.3. Health Risk from Airborne Lead Particulates. Estimated Number of Persons at Excess Risk, as Defined by a Continuous Blood Level in Excess of 60 µg/dl of Whole Blood†¹

Site	Ranges of Lead Concentrations† ² (µg/m ³)	Total Exposed Population	Annual Level of Risk		
			Estimated Number of Persons at Risk† ³ (annualized)		Normalized Response† ⁴
Iron County, MO	0.356-3.270 ^H 0.356-1.743 ^L	326,657	Total	2.39-3.29	-
			Background	2.22	-
			Increment	0.26-1.07	(0.080-0.327)×10 ⁻⁵
Sussex County, NJ	0.353-0.368 ^H 0.353-0.360 ^L	26,306,662	Total	179-179	-
			Background	179	-
			Increment	0	0
Palmerton, PA	0.354-0.391 ^H 0.354-0.441 ^L	12,765,353	Total	86.8-88.0	-
			Background	87.2	-
			Increment	0.6-0.8	(0.48-0.59)×10 ⁻⁷
Corpus Christi, TX	0.353-0.392 ^H 0.353-0.373 ^L	993,708	Total	6.78-6.82	-
			Background	6.79	-
			Increment	0-0.13	(0-0.013)×10 ⁻⁵
Background Reference	0.353				

†¹ A minimal definition of lead intoxication.

†² H refers to seasonal high. L refers to seasonal low. Corresponding isopleth graphs are identified by season in the text. A single background lead concentration is used for all sites. Concentrations presented are total airborne lead concentrations (background + increment).

†³ Values represent number of persons at risk of developing Pb-B ≥ 60 µg/dl from exposure to (1) total airborne lead (battery industry + background), (2) a background air lead concentration, and (3) incremental air lead concentrations due to battery industry alone. The range of response represents seasonal variation in exposure levels, as in Table 6.1.

†⁴ Normalized response is obtained by dividing "Persons at Risk" by "Total Exposed Population." This value gives a measure of individual risk due to incremental lead exposure from the battery industries, and can be compared to the individual risk coefficient for exposure to the background lead concentration, 0.68×10^{-5} .

by subtracting a normal probability value for a reference population from that derived for the exposed populations. Thus, the model assumes a background level of cadmium exposure present in the environment. It also assumes that additional cadmium exposure will result in an upward shift in mean concentrations of cadmium in the kidney for a population such that the individual risk for clinically defined tubular proteinuria is increased. A conservative risk estimate was made using an epidemiological definition of tubular proteinuria based on the upper 95% confidence interval of a reference population.⁴⁰ A daily cadmium dose to the body can be calculated from ambient exposure levels, through multiplication of the ambient exposure levels by the appropriate absorption and retention rates.⁴¹ Details of the model are presented in the earlier HEED (ANL/ES-105).

In the analysis presented in Table 6.4, a first order estimate has been made of the excess risk of developing tubular proteinuria from ground-level exposure to cadmium. For each of the four specific sites analyzed in Section 4, for airborne cadmium concentrations in the vicinity of primary zinc smelters, risk coefficients were derived. For each site, the seasonal high and associated isopleth values, and the seasonal low and associated isopleth values were examined. Cadmium isopleth values with a risk coefficient insignificantly different from background were deleted from further analysis. The area in square kilometers between isopleth lines was approximated for each seasonal high and seasonal low for the remaining isopleths. The population densities for these areas were estimated from county-level demographic information.^{42,43} For each cadmium exposure level, the possible number of persons affected at the end of 30 years was estimated by the equation:

$$\text{number of persons} = \text{area (km}^2\text{)} \times \frac{\text{population density}}{\text{km}^2} \times \text{risk coefficient.}$$

These values were summed over the appropriate cadmium exposure levels for the areas between retained isopleth lines at each industrial site, once for the seasonal highs and again for the seasonal lows. The areas with cadmium concentrations above background differed for the high and low analysis. Hence, we present a range for the size of the area at risk (Table 6.4, column 3). As can be seen, there is considerable variation in the risk due to changes in the affected area size with seasonal weather variations. The range in

Table 6.4. Estimated Number of Persons at Excess Risk to Tubular Proteinuria from 30 Years Exposure to Various Levels of Cadmium (annualized).¹

Location	Range of Cadmium Concentrations, by Season, ng/m ³	Coefficient of Excess Risk of Tubular Proteinuria ²	Approximate Area at Risk ³ km ²	Total Exposed Population ⁴	Estimated Number of Persons at Excess Risk Resulting from 30 Years Exposure (annualized)
Missouri	7.6 - 15.10 ^H 7.6 - 11.27 ^L	0 - 0.0022 0 - 0.0015	21,517- 18,259	326,657	0 - 12
New Jersey	7.696 ⁵	0 - 0.0007	757	26,306,662	0 - 14
Pennsylvania	8.5 - 34.30 ^H 8.0 - 26.90 ^L	0 - 0.0068 0 - 0.0056	32,400- 31,500	12,765,373	442 - 701
Texas	7.6 - 10.70 ^H 7.6 - 9.12 ^L	0 - 0.0011 0 - 0.0007	15,790- 10,459	993,708	0 - 11
Reference	7.5				

H = seasonal high

L = seasonal low

¹Because cadmium accumulates in the body over a period of years, it is anticipated that the level of risk would increase with the length of exposure. In addition, 30 years was used to be compatible with the previous HEED (ANL/ES-105).

²Range due to the use of standard errors from two separate control populations.

³Range due to seasonal variations in meteorology.

⁴Based on the following population densities: Missouri - 10.082/km², New Jersey - 811.934/km², Pennsylvania - 393.993/km², Texas - 30.67/km². Each total area is 32400 km² and this column includes persons in areas not at risk over background. The population was assumed to be constant over the 30-year analyses.

values is also due in part to the use of a standard error from two separate control populations.^{44,45}

The model estimates excess risk coefficients ranging from 0 to 0.0068. Pennsylvania is predicted to be the area with the largest excess risk coefficient and, due to the associated high population density, the number of persons estimated to be at risk at the end of thirty years appears significant. It should be remembered that this is an approximation, based on a very conservative definition of tubular proteinuria (290 μg β_2 -microglobulin per liter of urine).

6.2 OCCUPATIONAL HEALTH AND SAFETY

The occupational health and safety of workers in those industries required for large-scale production of zinc/halogen batteries is assessed by two different methods. The first method utilizes the toxicological models presented in Section 6.1 to predict responses to the several pollutants at exposure levels such as might be found in a typical industrial work area. Assumptions made regarding the number of days and hours worked and exposure levels encountered outside the work area are those described in Appendix A.4 of the HEED for Batteries--1980 (ANL/ES-105). The second method utilizes data from the U.S. Department of Labor, Bureau of Labor Statistics, on occupational injury rates, and, as such, addresses the issue of occupational safety.

6.2.1 Occupational Health

Sulfur Oxides and Particulates

The model used to estimate health effects of sulfur oxides and particulates was developed to analyze environmentally exposed populations. It does not apply to the occupational setting.

Vinyl Chloride

As indicated in the section on PVC, the vinyl chloride model was developed specifically for occupational exposures. The excess risk is approximately

2/100,000,000 angiosarcomas of the liver with a 35-year exposure to 1 ppm VC for 8 hr/day, 5 days/week.

Cadmium

As stated in the earlier HEED, the cadmium model is based on epidemiological studies of general population response to environmental exposures. Because of this, and the physiological reaction difference to the much higher levels seen in occupational exposures,⁴⁶⁻⁴⁸ the model is inappropriate for use with occupational exposures.

Lead

Application of the lead dose-response function to possible workplace exposure levels indicates that such exposures could result in a likelihood of 1 in 100 having a blood-lead level at or above 60 µg/ml, a low cutoff point for central nervous system dysfunction.

6.2.2 Occupational Safety

Listings of industries required for production of zinc/chloride and zinc/bromine batteries are presented in Tables 6.5 and 6.6. The Standard Industrial Classification (SIC) code number for each industry is also presented, along with incidence rates per 100 full-time workers for occupational injury (1975, 1977, 1978). Note that little change in incidence rates occurred over the four-year period covered; in general, industries with high incidence rates remained high, and those with low rates remained low. Incidence rates for the given battery-related industries are presented along with comparison rates for persons employed in (1) all industries in the general SIC category related to the battery industry (GRI) and (2) the general private sector (GP). This comparison approach asks the question: Are there particular, identifiable risks associated with employment in industries required for zinc/halogen battery production which are higher or lower than those that would be encountered by a similar work force employed in (1) a category of related industries requiring similar worker talent and experience and (2) the general population working in the private sector?

Table 6.5. Occupational Injury Rates for Industries Involved in Zinc/Chloride Battery Manufacture

Industry	Injury Incidence Rates ^a									SIC Industry Description and Code Number		
	SIC Code	Sector ^b	Total Cases	1975 Lost Workday Cases	1975 Lost Workdays	Total Cases	1977 Lost Workday Cases	1977 Lost Workdays	Total Cases		1978 Lost Workday Cases	1978 Lost Workdays
Zinc mining and milling	1031	SI GRI GP	6.5 10.9 8.8	4.4 5.6 3.2	69.2 111.9 54.4	7.4 10.8 9.0	4.5 5.9 3.7	83.9 128.3 60.0	9.9 11.3 9.2	5.4 6.4 4.0	113.1 142.3 62.1	Metal mining (10) Mining Private sector
Zinc primary smelting and refining	3333	SI GRI GP	14.1 16.7 8.8	8.6 6.2 3.2	132.5 112.9 54.4	12.1 15.7 9.0	5.0 6.6 3.7	110.1 115.9 60.0	12.7 16.5 9.2	5.8 7.3 4.0	108.9 120.5 62.1	Primary nonferrous metals (333) Primary metal industry (33) Private sector
Chlorine production	2812	SI GRI GP	6.6 6.7 8.8	1.8 2.2 3.2	49.5 47.5 54.4	4.9 6.2 9.0	2.2 2.4 3.7	50.8 49.9 60.0	4.9 5.8 9.2	2.3 2.4 4.0	54.3 48.4 62.1	Alkalies and chlorine (2812) Industrial chemicals (281) Private sector
Zinc chloride production	2819	SI GRI GP	7.0 6.7 8.8	2.3 2.2 3.2	49.2 47.5 54.4	5.8 6.2 9.0	2.2 2.4 3.7	43.7 49.9 60.0	5.5 5.8 9.2	2.1 2.4 4.0	40.0 48.4 62.1	Industrial inorganic chemicals, n.e.c. (2819) Industrial chemicals (281) Private sector
Hydrochloric acid production	2819	SI GRI GP	7.0 6.7 8.8	2.3 2.2 3.2	49.2 47.5 54.4	5.8 6.2 9.0	2.2 2.4 3.7	43.7 49.9 60.0	5.5 5.8 9.2	2.1 2.4 4.0	40.0 48.4 62.1	Industrial inorganic chemicals, n.e.c. (2819) Industrial chemicals (281) Private sector
titanium primary smelting and refining	3339	SI GRI GP	16.3 14.1 8.8	8.5 5.5 3.2	172.0 132.5 54.4	13.2 12.1 9.0	5.0 5.0 3.7	75.6 110.1 60.0	13.4 12.7 9.2	5.7 5.8 4.0	95.6 108.9 62.1	Primary nonferrous metals, n.e.c. (3339) Primary nonferrous metals (333) Private sector
Polyvinyl chloride production	2821	SI GRI GP	7.9 6.7 8.8	2.6 2.2 3.2	41.5 47.5 54.4	8.5 6.2 9.0	3.3 2.4 3.7	52.0 49.9 60.0	7.9 5.8 9.2	3.5 2.4 4.0	51.4 48.4 62.1	Plastic materials and resins (2821) Plastic materials and synthetics (281) Private sector
Vinyl chloride monomer production	2869	SI GRI GP	na na --	na na --	na na --	4.8 5.8 9.0	1.9 2.3 3.7	31.0 41.8 60.0	4.4 5.6 9.2	1.9 2.3 4.0	31.6 39.1 62.1	Industrial organic chemicals, n.e.c. (2869) Industrial organic chemicals (286) Private sector
Fiberglass-reinforced polyester production	3079	SI GRI GP	15.3 15.2 8.8	4.9 6.6 3.2	75.9 112.1 54.4	16.8 16.1 9.0	6.4 7.4 3.7	92.5 112.9 60.0	17.5 16.6 9.2	7.0 7.9 4.0	102.0 121.7 62.1	Miscellaneous plastic products (307) Rubber and miscellaneous plastic products (28) Private sector
Polyester resin monomer production (anhydrides, glycols, styrene)	2865 2869	SI GRI GP	7.5 10.9 8.8	2.6 3.9 3.2	45.4 65.6 54.4	5.8 7.3 9.0	2.3 2.9 3.7	41.8 48.0 60.0	5.6 7.2 9.2	2.3 3.1 4.0	39.1 48.9 62.1	Industrial organic chemicals (286) Chemicals and allied products (28) Private sector
Fiberglass production	1446	SI	5.9	3.5	45.0	5.1	3.3	58.0	6.8	4.1	87.4	Nonmetallic minerals, except fuels (14) Mining Private sector
Industrial sand mining		GRI GP	10.9 8.8	5.6 3.2	111.9 54.4	10.8 9.0	5.9 3.7	128.3 60.0	11.3 9.2	6.4 4.0	142.3 62.1	
Glass production	3229	SI GRI GP	11.0 14.0 8.8	3.1 5.0 3.2	63.1 97.1 54.4	12.6 14.2 9.0	4.3 6.3 3.7	73.0 125.3 60.0	12.7 14.2 9.2	5.1 7.3 4.0	78.0 130.8 62.1	Pressed and blown glass, n.e.c. (3229) Glass and glassware, pressed or blown (322) Private sector

^aIncidence rates represent the number of injuries and lost workdays per 100 full-time workers in the years indicated, as calculated and tabulated in U.S. Department of Labor, Bureau of Labor Statistics, Bulletin 1981 (1978) and Bulletin 2078 (1980).

^bSI, GRI, and GP refer to specific industry, general related industry, and general population, respectively. The SIC industry description and code number used for these industry definitions are shown in the last column of the table.

Table 6.6. Occupational Injury Rates for Industries Involved in Zinc/Bromine Battery Manufacture

Industry	Injury Incidence Rates ^a											SIC Industry Description and Code Number
	SIC Code	Sector ^b	1975			1977			1978			
			Total Cases	Lost Workday Cases	Lost Workdays	Total Cases	Lost Workday Cases	Lost Workdays	Total Cases	Lost Workday Cases	Lost Workdays	
Zinc mining and milling	1031	SI GRI GP		-	c		-	c		-	c	Metal mining (10) Mining Private sector
Zinc primary smelting and refining	3333	SI GRI GP		-	c		-	c		-	c	Primary nonferrous metals (333) Primary metal industry (33) Private sector
Bromine production	2819	SI GRI GP	7.0 6.7 8.8	2.3 2.2 3.2	49.2 47.5 54.4	5.8 6.2 9.0	2.2 2.4 3.7	43.7 49.9 60.0	5.5 5.8 9.2	2.1 2.4 4.0	40.0 48.4 62.1	Industrial inorganic chemicals, n.e.c. (2819) Industrial chemicals (281) Private sector
Zinc bromide production	2819	SI GRI GP	7.0 6.7 8.8	2.3 2.2 3.2	49.2 47.5 54.4	5.8 6.2 9.0	2.2 2.4 3.7	43.7 49.9 60.0	5.5 5.8 9.2	2.1 2.4 4.0	40.0 48.4 62.1	Industrial inorganic chemicals, n.e.c. (2819) Industrial chemicals (281) Private sector
Chlorine production	2812	SI GRI GP		-	c		-	c		-	c	Alkalies and chlorine (2812) Industrial chemicals (281) Private sector
Polypropylene production	2821	SI GRI GP	7.9 6.7 8.8	2.6 2.2 3.2	41.5 47.5 54.4	8.5 6.2 9.0	3.3 2.4 3.7	52.0 49.9 60.0	7.9 5.8 9.2	3.5 2.4 4.0	51.4 48.4 62.1	Plastic materials and resins (2821) Plastic materials and synthetics (281) Private sector
Carbon black production	2895	SI GRI GP	13.8 10.5 8.8	4.0 3.5 3.2	113.2 54.1 54.4	9.7 12.0 9.0	3.3 4.6 3.7	86.9 77.6 60.0	7.2 11.0 9.2	4.3 4.9 4.0	86.5 71.8 62.1	Carbon black (2895) Miscellaneous chemical products (289) Private sector
Polyvinyl chloride production	2821	SI GRI GP		-	c		-	c		-	c	Plastic materials and resins (2821) Plastic materials and synthetics (281) Private sector
Battery complexing agent production	2869	SI GRI GP	na na --	na na --	na na --	4.8 5.8 9.0	1.9 2.3 3.7	31.0 41.8 60.0	4.4 5.6 9.2	1.9 2.3 4.0	31.6 39.1 62.1	Industrial organic chemicals, n.e.c. (2869) Industrial organic chemicals (286) Private sector
Chlorethanol production	2869	SI GRI GP	na na --	na na --	na na --	4.8 5.8 9.0	1.9 2.3 3.7	31.0 41.8 60.0	4.4 5.6 9.2	1.9 2.3 4.0	31.6 39.1 62.1	Industrial organic chemicals, n.e.c. (2869) Industrial organic chemicals (286) Private sector
Teflon production	2821	SI GRI GP	7.9 6.7 8.8	2.6 2.2 3.2	41.5 47.5 54.4	8.5 6.2 9.0	3.3 2.4 3.7	52.0 49.9 60.0	7.9 5.8 9.2	3.5 2.4 4.0	51.4 48.4 62.1	Plastic materials and resins (2821) Plastic materials and synthetics (281) Private sector

^aIncidence rates represent the number of injuries and lost workdays per 100 full-time workers in the years indicated, as calculated and tabulated in U.S. Department of Labor, Bureau of Labor Statistics, Bulletin 1981 (1978) and Bulletin 2078 (1980).

^bSI, GRI, and GP refer to specific industry, general related industry, and general population, respectively. The SIC industry description and code number used for these industry definitions are shown in the last column of the table.

^cRefer to listings in Table 6.5 for rates for these industries.

The industries required for zinc/chloride and zinc/bromine battery production are categorized in Tables 6.7 and 6.8, respectively, according to whether they have incidence rates (1) less than or equal to those for persons in the general private sector, (2) greater than those for the private sector and approximately equal to those for persons employed in the general related SIC category and (3) greater than those for persons employed in both the private sector and in the general related SIC category.

Analyzing the industries required for zinc/chloride battery production (Tables 6.5 and 6.7), we see that most industries producing the materials required for battery manufacture have occupational injury rates close to the mean for the entire private sector. For these industries, expansion to meet the needs of a growing market for zinc/chloride batteries would not produce a workforce with increased incidence of occupational injury. On the contrary, if persons were pulled from industries with higher injury incidence rates, the mean incident rate for the new work force might be lowered. Injury incidence rates for zinc primary smelting and refining, titanium primary smelting and refining, and fiberglass-reinforced polyester production, are higher than those for the entire private sector, but are similar to those for industries in the general related categories of primary metals industries (SIC 33), and rubber and plastic products, nec(SIC 30), respectively. If primary smelting and refining industries for zinc and titanium were to increase 11% and 55% in size to meet the needs of producing 1×10^6 battery modules per year (Table 2.11), and if workers were pulled from other primary metal industries to meet these needs, not much change in occupational injury rates would be experienced. The same is true for fiberglass-reinforced polyester production. Since no industries are categorized as having occupational injury incidence rates greater than those for the general related industries (GRI), no predictable increases in occupational injury rates are anticipated to accompany expanded production of zinc/chloride batteries. One reason inherent in this conclusion is the assumption made in Section 2 that zinc from the zinc/chloride batteries will not be recycled. If the zinc were to be recycled via secondary smelters, an industry would be required (secondary zinc smelting) that has occupational injury rates higher than those for both the entire private sector and the general related-primary metals industries.

Table 6.7. Categorization of Industries Involved in Manufacture of Zinc/Chloride Batteries According to Incidence Rates for Occupational Injury

Battery System	Incidence Rates < GP† ¹	GP > Incidence Rates \cong GRI† ¹	Incidence Rates < GRI† ¹
Zinc/chloride	Zinc mining and milling	Zinc primary smelting and refining	none
	Chlorine production	Titanium primary smelting and refining	
	Zinc chloride production	Fiberglass-reinforced polyester production	
	Hydrochloric acid production		
	Polyvinyl chloride production		
	Vinyl chloride production		
	Polyester resin monomer production		
	Fiberglass production		

†¹ GP and GRI refer to general population and general related industries, as in Table 6.5. Actual incidence rates for the categorized industries are given in the latter table.

Table 6.8. Categorization of Industries Involved in Manufacture of Zinc/Bromine Batteries According to Incidence Rates for Occupational Injury

Battery System	Incidence Rates \leq GP ^{†1}	GP < Incidence Rates \cong GRI ^{†1}	Incidence Rates > GRI ^{†1}
Zinc/bromine	Zinc milling and milling	Zinc primary smelting and refining	Carbon black production (1975)
	Bromine production	Carbon black production (1977, 1978)	
	Zinc bromide production		
	Chlorine production		
	Polypropylene production		
	Polyvinyl chloride production		
	Battery complexing agent production		
	Chlorethanol production		
	Teflon production		

^{†1} GP and GRI refer to general population and general related industries, as in Table 6.6. Actual incidence rates for the categorized industries are given in the latter table.

Turning to the rates for industries producing materials required for zinc/bromine battery manufacture (Tables 6.6 and 6.8), a similar conclusion is drawn as that for the zinc/chloride battery system; i.e., no predictable increases in occupational injury rates are anticipated to accompany expanded production of zinc/bromine batteries. Carbon black production in 1975 had a rate of lost work days (113 days per 100 full-time employees), that was considerably higher than the means for the general related industries (54 days per 100 full-time employees) and for the entire private sector (54 days per 100 full-time employees). In 1977 and 1978, however, the lost workday incidence for the carbon black industry was similar to those for the two comparison categories (Table 6.6). This industry has not therefore been singled out as a high risk industry with respect to occupational injuries.

Table 6.9 presents an estimate of the number of persons that would be employed to produce the amount of material required for making 1×10^6 zinc/chloride battery modules per year (Table 2.11, Section 2). These estimates were obtained in two ways.

In the cases of primary zinc and of chlorine production, all persons employed in the indicated SIC industry category are involved in production of the required materials (primary zinc and chlorine). The fraction of total workers in the SIC category that would be used for battery material production was therefore assumed to be the same as the fraction of total U.S. production represented by the amount of material required. For example, 50,000 MT of primary zinc is required for making 1×10^6 zinc/chloride battery modules, representing 11% of the U.S. annual production. The total number of persons employed in SIC category 3333 (primary smelting and refining of zinc) is 5.2×10^3 (Table 6.9), and 11% of that number is 570 persons employed to produce 50,000 MT of primary zinc per year. The estimate for chlorine production was made in a similar way.

For the other industries, the estimates were less straightforward, since persons listed as employed in the other SIC categories are employed in many related industries, only one of which is the industry making the materials required for zinc/chloride battery production. The estimate used is based on the assumption that, for a given SIC category of industries, all of which make

Table 6.9. Estimate of Number of Persons Employed and Annual Injury and Fatality Cases Occurring during Production of Materials Required for 1×10^6 Zinc/Chloride Battery Modules.

Material	Amount Required ^a (MT/ 10^6 modules)	Unit Value of Material (\$/lb)	Total Value of Material ^d (\$ $\times 10^{-6}$) (A)	Persons Employed Per Unit Value of Product (1972) ^e				Estimate of Persons Employed to Produce Material Required ^f (AxD)	Estimated Total Annual Injury Cases ^h			Estimated Total Annual Fatalities ⁱ
				SIC Code	Persons Employed ($\times 10^{-3}$) (B)	Value of Shipments (\$ $\times 10^{-6}$) (C)	Ratio B $\times 10^3$ /C (persons/ 10^6 \$) (D)		Total Cases	Lost Workday Cases	Lost Workdays	
Primary zinc (3333)	50,000 (11)	-	-	3333	5.20	-	-	570 ^g	72	33	620	0.04
Zinc chloride (2819)	100,000 (470)	0.15 (1972) ^b	33.1 (1972)	2819	63.8	3830	16.7	550	30	12	220	0.04
Vinyl chloride monomer (2869)	70,000 (2.5)	0.04 (1969) ^c	6.2 (1969)	2869	102	9220	11.1	70	3	1	22	0.005
Chlorine (2812)	50,000 (0.50)	-	-	2812	13.3	823.6	16.1	70 ^g	3	2	38	0.005
Polyvinyl chloride (2821)	70,000 (2.5)	0.14 (1969) ^c	21.6 (1969)	2821	54.8	4480	12.2	260	21	9	133	0.02
Hydrochloric acid (2819)	50,000 (1.9)	0.02 (1969) ^c	2.2 (1969)	2819	63.8	3830	16.7	40	2	1	16	0.003

^aData from Table 2.11, Section 2, this document. Numbers in parentheses are percentage of U.S. annual production represented by amount required.

^bChemical Marketing Reporter, September, 1972.

^cChemical Statistics Handbook, Seventh Edition 1971, Manufacturing Chemists Association, Washington, DC.

^dCalculated by converting MT to pounds for material required, column 1, and multiplying by price per pound in column 2. Values are for 1969 or 1972, to correspond to year of values in Ratio D (persons employed per 10^6 dollars), column 4D.

^eData from Tables 6A, 1972 Census of Manufacturers, U.S. Bureau of Census, U.S. Government Printing Office, Washington, DC. Ratio D gives number of persons employed per dollar value of product for the given SIC grouping of industries in 1972.

^fEstimate obtained by multiplying Ratio D (number of persons employed per 10^6 dollars of product value produced by a given SIC industry grouping for 1972) times A, the dollar value ($\times 10^{-6}$) of the material required for battery production (column 3), except where indicated otherwise.

^gFor primary zinc (3333) and chlorine (2812), persons employed to produce material required were calculated from total number of persons employed in the SIC code grouping, times the fraction of U.S. annual production represented by the amount of material required (column 1, parentheses), since all persons in the SIC code grouping are involved in producing the material required.

^hCalculated by multiplying injury incidence rates (values per 100 full-time employees) listed in Table 6.5, by the estimate of persons employed (divided by 100).

ⁱThe fatality incidence rate (1975) for the Manufacturing Industries category (0.07 fatalities per 1000 full-time employees) was multiplied by the estimated workforce size (divided by 1000). Fatality rates were obtained from Bulletin 1981, Bureau of Labor Statistics, U.S. Department of Labor.

related products, the number of persons employed per dollar value of product for the general SIC category of industries (Ratio D, Table 6.9, Column 4) is similar to that for the specific industry required for battery production. This assumption appears to be acceptable for those cases where a comparison of Ratio D for the general industry category (GI) and a specific industry category (SI) can be made, as shown below.

<u>SIC Code</u>	<u>Persons Employed ($\times 10^{-3}$)</u>	<u>Ratio D</u>
GI 2869	102	11.1
SI 28692	79	10.7
GI 2812	13.3	16.4
SI 28121	0.2	14.7
GI 2819	63.8	16.7
SI 28194	1.4	17.0

Ratios D for the general and specific industry categories are similar even when the number of persons employed in the specific SIC category is very small compared to the number employed in the general category, as in the case of chlorine (2812) and hydrochloric acid (2819) production. Given that the latter assumption is acceptable, the remaining calculation is fairly straightforward. The number of persons employed per 10^6 dollars of value produced (Ratio D), is multiplied by the total value of the material required for battery production (Table 6.9, column 3).

It can be seen from Column 5, Table 6.9, that of the industries listed, zinc primary smelting and refining, zinc chloride production, and polyvinyl chloride production are the industries requiring the largest number of employees for production of materials for zinc/chloride battery manufacture. Zinc primary smelting and refining is the industry with the largest estimated total occupational injury cases (Table 6.9, Column 6), due to the relatively large number of persons estimated to be employed, and the relatively higher rates of occupational injury compared to other industries (Table 6.5). Summing injury cases for all industries analyzed, it is estimated that a total of 131 occupational injury cases may occur annually in a workforce of 1560 persons during production of materials required for 10^6 zinc/chloride battery modules per year. (Note that not all industries required for zinc/chloride battery production (Table 2.11) are analyzed for number of employees, due to lack of required data).

In the final column of Table 6.9 are listed total annual fatalities for the workforce size under consideration, estimated by multiplying the number of persons employed (Column 5), by the fatality incidence rate for the Manufacturing Industries category (0.07 per 1000 full-time employees in 1975). It can be seen that the number of anticipated annual fatalities due to occupational injuries is low. Considering a 50-year period of production, and summing the estimated fatalities for the industries listed, 5 to 6 fatalities might occur over 50 years during production of materials required for annual production of 1×10^6 zinc/chloride battery modules. This latter estimate assumes that industry characteristics, such as injury rates and numbers of persons employed per amount of material produced, do not change dramatically over the 50 year period considered. In spite of this limitation, it does allow a general comparison of annual numbers of injuries (Column 6), and fatalities (Column 7) estimated for the occupational workforce required for zinc/chloride battery production, with the numbers of persons expected to be adversely affected by environmental releases of pollutants (Sec. 6.1, Tables 6.1-6.4).

6.3 ADDITIONAL BATTERY COMPONENTS

6.3.1 Chlorine

Potential health effects of human exposure to chlorine as a result of increased use of electric vehicles powered by zinc/chloride batteries needs to be evaluated. To do this, concentrations of chlorine that might be encountered in various accident scenarios are presented in tabular form, based on a hazard assessment report by R. Zalosh et al.⁴⁹, in which actual chlorine concentrations in a simulated accident situation were measured. Responses to chlorine at concentrations relevant to potential accident scenarios are then presented based on available data for both man and other animal systems.

Acute Exposure to Chlorine

Key chlorine concentrations estimated for various accident scenarios in which acute exposure to high concentrations of chlorine might occur are summarized in Table 6.10. Health effects questions related to these potential

Table 6.10. Acute Chlorine Exposure Conditions and Corresponding Health Responses
Estimated for Several Accident Scenarios Involving Electric Vehicles
Powered by Zinc/Chloride Batteries^a

Exposure Event	Estimated Chlorine Concentration	Estimated Exposure Time	Estimated Exposure Area and Exposure Conditions	Estimated Responses		
				Man	Dog	Mouse
1. Chlorine hydrate spill ^b	>30-50ppm avg. with >100ppm spikes (>5 spikes/min.) ^c	First 10 to 20 min. after spill (10-20 min. exposure)	-From 7.6 to 23m downwind -30° sector angle -33° C road temp. -1-4m/sec. wind speed	-Severe eye and respiratory tract irritation (40)	-Severe eye and respiratory tract irritation	-Severe eye and respiratory tract irritation
	3-15ppm avg. with 10-80ppm spikes (<2 spikes/min.)	From 20 to 50 min. after spill (30 min. exposure)	-At 7.6m downwind	-Incapacitation in few seconds (48)	-Death unlikely (56)	-Death possible in <50% of mice (75,76)
	0-7ppm avg. with 2-80ppm spikes (<2 spikes/min.)	From 20 to 50 min. after spill (30 min. exposure)	-At 23m downwind	-Death possible		
2. Forty liter/minute continuous vapor release outdoors ^d	≥100ppm	30 min. or more ^e	-To 30m downwind -2m/sec wind speed -At 0.3m above ground	-Severe eye and respiratory tract irritation (48)	-Severe eye and respiratory tract irritation	-Severe eye and respiratory tract irritation
	≥100 ppm	30 min. or more ^e	-To 6m downwind -5m/sec wind speed -At 0.2m above ground	-Incapacitation in few seconds (48)	-Death possible depending on length of exposure	-Death in 50% of mice after 30 min. at 100ppm (75,76)
					-Death unlikely for 30 min. exposure (56)	
3. Twenty-eight liter instantaneous vapor release outdoors ^e	≥1000ppm	2 sec ^g	-At 20m downwind ^g	-Acute, transient eye and respiratory tract irritation -Death unlikely due to very short exposure time		
	≥100ppm	4 sec ^g	-2m/sec wind speed -At 20m downwind ^g			
	≥100ppm	6 sec ^g	-5m/sec wind speed -From 60 to 120m downwind ^g			
	≥100ppm		-2m/sec wind speed			
4. Chlorine release in longitudinally ventilated tunnel ^h						
	40 liter/min. continuous vapor release	2-5 ppm avg. ^f	30 min. or more ^e	>200m from accident site ^l	-Moderate eye and respiratory tract irritation -Unbearable in 20 min. (67)	-Data not located
	Small hydrate spill	<1 ppm avg. ^f	<20 min. ^j	>200m from accident site ^l	-Slight irritation in some	-Data not located
	Large hydrate spill	10-20 ppm avg. ^f	<20 min. ^j	>200m from accident site ^l	-Moderate to severe eye and respiratory tract irritation -Death unlikely	-Data not located
5. Forty-one kilogram instantaneous vapor release outdoors ^k	≥50 ppm	17 sec ^g	-At 300m downwind ^g -5m/sec wind speed	-Severe irritation -Death unlikely	-Same as human	-Same as human
	≥50 ppm	70 sec ^g	-At 1200m downwind ^g -2m/sec wind speed	-Severe irritation -Death possible depending on volume of 1000ppm isopleth	-Same as human	-Same as human

Table 6.10 Footnotes

- ^aData in columns 1 through 4 are from R. Zalosh et al., "Hazard Assessment of Zinc-Chlorine Electric Vehicle Batteries", (49). Refer to Appendix B for more detailed presentation and analysis of this information. In the latter report, exposure event 1 was evaluated via actual hydrate spill experiments and accompanying dispersion calculations. Exposure events 2 through 5 were evaluated via dispersion calculations only. Health responses in this table are estimated based on data in Figure 6.2 and on data in indicated references.
- ^bExposure caused by rupture of battery case and store wall from collision, piercing, or uncontrollable pressure increase. Data corresponded to spill of hydrate containing 10-20 kg chlorine (25-50% charge) onto a 33°C road surface with 1-4 m/sec wind speed. Concentrations were experimentally determined.
- ^cConcentrations presented are minima, since most spikes of chlorine concentration in the first 20 minutes after the spill exceeded the 100 ppm detection limit of the analyzers.
- ^dExposures caused by breaching of chlorine flow lines while maintaining chlorine pump operation. Chlorine is pumped at 40 L/min. during battery discharge, and at 28 L/min. during charge. Event analyzed therefore corresponds to maximum anticipated continuous release rate. Concentrations are based on dispersion calculations.
- ^eTime of exposure would depend on time to pump shut-down or to depletion of chlorine supply. At full charge the chlorine content of the battery is 41 kg (1.3×10^4 liters, STP). At a pump rate of 40 L/min., continuous chlorine release would deplete 10% of a 41-kg store in ~30 minutes.
- ^fExposures caused by breach of the cell stack compartment with release of the 28 liters (1 ft³) of chlorine present in the vapor space of the battery cell stack. Dispersion calculations were based on an expanding puff model.
- ^gExposure to the indicated concentrations are short and transient due to the movement of a small chlorine puff past the indicated exposure point at the indicated wind speed. Estimated exposures are presented for locations where the exposure time at the indicated concentration is maximum, since the puff at that concentration has achieved a maximum volume.
- ^hExposures caused by accidental releases of chlorine as in events 1 and 2 above, except with accidents occurring inside a longitudinally ventilated tunnel (3-6 m/sec tunnel ventilation velocity).
- ⁱAverage tunnel concentrations were calculated for distances >200 m (>70 car lengths) from the accident site. Concentrations at the scene of the accident would be more similar to those presented for events 1 and 2.
- ^jThe rate of chlorine release from the accident site might be expected to decrease significantly after ~29 min, as in the case of the experimental hydrate spills (event 1). This would cause average tunnel concentration to decline after ~20 min also.
- ^kExposures caused by internal or external explosion resulting in instantaneous release of the entire store of chlorine from the fully-charged battery (41 kg).

exposures include: 1) What are the effects of exposure to > 30-50 ppm of chlorine for 10 to 20 minutes at the scene of an accident involving a large-scale chlorine hydrate spill? 2) How long can a person survive exposure to ≥ 50 ppm chlorine? ≥ 100 ppm chlorine? 3) Are there long-term effects of chlorine in survivors of acute exposure experiences? 4) At what concentrations is an irritation response to chlorine not likely to be accompanied by death? To try to answer these questions, data on responses to acute exposure to chlorine at high concentrations are presented below and analyzed with respect to the accident scenarios described.

Chlorine is a pungent, yellow-green gas (at normal temperatures and pressures), with a density 2.5 times that of air. It is a strong irritant to mucous membranes of the respiratory tract and eyes. Human responses following exposure to high levels of chlorine have been characterized from two sources: (1) reports of effects, and after-effects, of gassing during World War I⁵⁰⁻⁵²; and (2) case reports of accidental exposures in industry and elsewhere.⁵³⁻⁵⁷ These sources indicate that signs and symptoms of acute exposure in humans to high levels of chlorine are: immediate bronchoconstriction; coughing and choking; anxiety, sensation of suffocation, vomiting, retching; burning of nose, pharynx and respiratory tract; dyspnea (shortness of breath); conjunctival injection; hemoptysis (bleeding from lungs); cyanosis. Active respiratory tract irritation can in some cases cause immediate fainting, unconsciousness, and death. When death is not immediate but occurs within 24 hours, pulmonary edema is accompanied by plasma loss, hemoconcentration, anoxemia, acidosis, cyanosis, decreased body temperature, increased pulse rate, decreased blood pressure, all leading to shock at death. Those who survive forty-eight hours usually recover.⁵² Clinical findings shortly after an acute exposure are: slight X-ray changes; pulmonary edema; early transient leucocytosis; slight fever; tracheobronchitis; lung function changes including decreased VC, FRC, P_{aO_2} , and TLC.

Respiratory symptoms among survivors of acute exposures have been reported to persist for as short as 30 days⁵⁸ to as long as 18 to 20 months.⁵⁷ Reports on the existence of long-term effects of acute exposure to chlorine are conflicting. Joyner and Durel⁵⁶ reported on a 36-ton chlorine spill in Louisiana where approximately 100 persons were treated for chlorine exposure. At seven

years, a follow-up study was conducted on twelve of the most severely effected patients.⁵⁹ At this time, measurements of respiratory function (TLC, VC, RV, FEV/1*) were all within two standard deviations of predicted values, chest X-rays were normal, and persons were asymptomatic from a respiratory standpoint. Kowitz et al.,⁵⁷ on the other hand, presented data supporting the existence of long-term lung changes in the form of decreased vital capacity, increased elastic work of breathing, and decreased diffusing capacity during a three-year period following acute exposure to chlorine among a group of accidentally exposed longshoremen.

The question remains, at what levels do humans respond to acute chlorine exposure as described above? What concentrations of chlorine are lethal to man after how long an exposure? Figure 6.2 presents pertinent data on this subject. Experimental studies on acute toxicity of chlorine are most extensive in the dog and mouse. Two studies reported that 85 to 90% of 23⁶⁰ or 22⁶¹ dogs died within three days of a 30-minute exposure to 800 to 900 ppm chlorine (Fig. 6.2). Only 50% of the 18 dogs exposed to chlorine for 30 minutes at a concentration of 700 to 800 ppm died within three days⁶⁰. At concentrations below 300 ppm, chlorine did not cause deaths among dogs exposed for 30 minutes.⁶⁰⁻⁶² At concentrations ten-fold below this (24 to 30 ppm), dogs exposed for 30 minutes experienced lacrimation (tearing of eyes), profuse salivation, as well as mild retching and vomiting.⁶¹ The mouse appears to be somewhat more sensitive than the dog to the acute effects of high-level chlorine exposure. Fifty percent of mice of three different strains died within four days of a 30-minute exposure to chlorine at 100-150 ppm.⁶³ In man, descriptions of responses to measured levels of chlorine are less readily available. In a report on medical aspects of chemical warfare (Ref. 52, p. 70), Vedder listed 100 ppm chlorine as the "approximate concentration to incapacitate a man in a few seconds owing to sensory irritation of the eyes (lachrymation) or upper respiratory passages (pain, coughing)," and also the "approximate concentration which if breathed for more than one or two minutes would cause definite bronchial or pulmonary lesions." Fieldner et al.⁶⁴ listed 40 to 60 ppm chlorine as dangerous to life after 30 to 60 minutes exposure, and 1000 ppm as likely to

* VC = vital capacity; FRC = functional residual capacity; P_{aO_2} = partial pressure of oxygen in arterial blood; TLC = total lung capacity; RV = residual volume; FEV 1 = forced expiratory volume at 1 second.

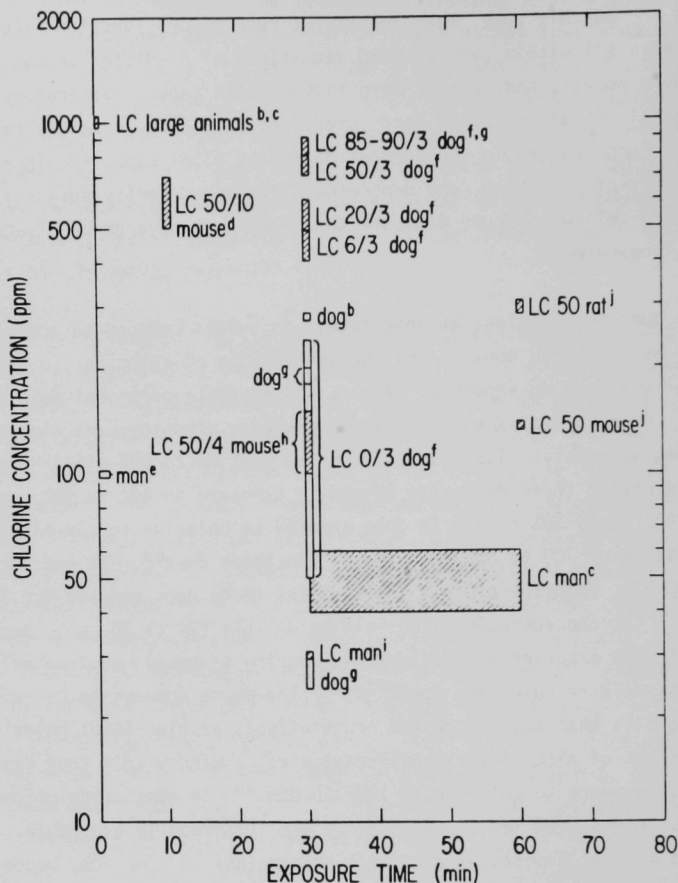


Fig. 6.2. Conditions of Acute Exposure to Chlorine and Corresponding Health Effects. Cross-hatched boxes indicate chlorine exposure conditions (concentration range and exposure time) under which death was observed in animals, or has been listed as likely for man. Open boxes indicate conditions under which severe eye and respiratory tract irritation are anticipated but death is unlikely. For cross-hatched boxes, species and LC A/B are shown. LC A/B indicates lethal concentration (for indicated exposure time) at which A percent of the animals died by the end of B days, where known. References for data are indicated by superscript. ^bFlury and Zernik⁶² ^cFieldner, et al.⁶⁴ ^dSilver and McGrath,⁷⁹ and Silver, et al.⁸⁰ ^eVedder,⁵² ^fUnderhill,⁶⁰ ^gBarbour,⁶¹ ^hSchlagbauer and Henschler,⁶³ ⁱZielhuis.⁶⁵ ^jFairchild, et al.⁶⁷

be fatal after a few deep breaths. Zielhuis⁶⁵ listed exposure for 30 minutes to 30 ppm chlorine as potentially lethal to humans. The ILDH is listed at 25 ppm (concentration immediately hazardous to life and health) in the NIOSH/OSHA Pocket Guide to Chemical Hazards.⁶⁶ On the other hand, the Registry of Toxic Effects of Chemical Substances⁶⁷ listed exposure for 30 minutes to 430 ppm chlorine as the LD_{LO} (low lethal dose) for man, a value closer to responses measured in dogs. Original data to document the validity of the human listings mentioned was not located.

In summary, 30-minute exposures of dogs at \cong 300 ppm chlorine or lower did not prove to be lethal; 30-minute exposures at 500 ppm chlorine or higher was lethal to significant fractions of the exposed dogs. The mouse appears to be more sensitive than the dog. The LC 50/4 for three strains of mice was 100-150 ppm following a 30-minute exposure. Human listings indicate that man may also be more sensitive than dogs, with lethal doses for man listed from 30 to 60 ppm chlorine for a 30-minute exposure time.

The data presented in Figure 6.2 for acute exposure responses to chlorine have been used, as shown in Table 6.10, column 4, to estimate responses in humans, dogs, and mice to chlorine concentrations anticipated for various accident scenarios.

Chlorine Hydrate Spill

It can be seen that a large chlorine hydrate spill (exposure event 1, Table 6.10) could possibly result in deaths from chlorine exposure for those trapped in the vicinity of an accident to 23 m (\sim 7 car lengths) downwind from the spill sight. If, however, humans are not more sensitive than dogs to acute chlorine exposure, death in this exposure area would be less likely due to the short exposure times anticipated for spills onto the 33°C pavement. In any case, able persons in this area would be forced to evacuate due to severe respiratory distress. In their analysis of the number of deaths anticipated from accidents involving chlorine hydrate spills, Zalosh et al.⁴⁹ concluded that "the expected fatality rates due to accidental chlorine releases in zinc/chloride battery-powered vehicles are comparable to internal combustion engine fatality rates (due to motor vehicle fire and carbon monoxide asphyxi-

ations) in conventional vehicles." Their calculational analysis took into account differences in anticipated chlorine fatalities due to differences in hydrate spill area, temperature of road surface, and wind conditions. It defined the number of persons at risk of death as the number of entrapments, plus incapacities currently experienced with conventional vehicles, and thus did not include consideration of otherwise able-bodied persons in the vicinity of the accident incapacitated due to chlorine exposure itself. It should be pointed out that responses in any case would vary with the age and the condition of the respiratory systems of the exposed persons. Causes of late deaths among dogs who did survive a 30-minute exposure to chlorine were diagnosed as emphysema, pneumonia, and bronchiolitis obliterans.⁶⁸ Preexisting lung disease has been shown to increase the likelihood of death from exposure to chlorine at high concentrations.⁶⁹

Rupture of Chlorine Flow Lines

Release of chlorine at 40 L/min due to rupture of chlorine flow lines while maintaining operation of the chlorine pumps (exposure event 2, Table 6.10) was calculated to produce an area containing ≥ 100 ppm chlorine that would extend out to 30 meters (~ 10 car lengths) downwind from the accident when the wind speed is 2 m/sec. Since the zinc/chloride battery at full charge contains 41 kg (1.3×10^4 liters) of chlorine, release of chlorine at this rate could theoretically continue for 30 minutes with depletion of only 10% of the chlorine store if the pumps were not shut down. This concentration of chlorine would quickly incapacitate people within the 30-m distance from the accident site, with death possible if exposure to ≥ 100 ppm chlorine were long enough. Note that the cloud of chlorine was estimated to reach only 0.3 m (~ 1 ft) from the ground, possibly limiting the number of persons exposed to the full ≥ 100 ppm concentration.

Instantaneous Chlorine Release

Instantaneous release of 28 liters of chlorine (exposure event 3, Table 6.10) could occur due to rupture of the cell stack compartment with release of the chlorine residing in the 28-liter space above the cell stack. As shown in

Table 6.10, this volume of chlorine is small enough that even at a wind speed of 2 m/sec, exposure to high chlorine concentrations should be brief enough that resulting respiratory distress should not lead to death or to long-term effects.

Chlorine Release in a Tunnel

Chlorine concentrations following release in a tunnel (exposure event 4, Table 6.10) were estimated for several accident scenarios. Concentrations calculated were averages for the entire tunnel at distances greater than 200 m (≥ 70 car lengths) from the accident scene. Concentrations were low, though irritating, in the case of a 40-L/min continuous vapor release and a small hydrate spill. For a large hydrate spill, average tunnel concentrations were estimated at 10-20 ppm, a concentration range expected to produce moderate to severe irritation, with death unlikely for exposure times less than 30 min. Exposure concentrations within the 200-m distance from the accident site would be expected to be significantly greater than the calculated tunnel averages, and could be approximated by concentrations described in the vicinity of exposure event 1, Table 6.10.

The most drastic accident considered was the instantaneous release of all the chlorine in the full-charged zinc/chloride battery (41 kg), presumably due to an external or internal explosion. As shown in Table 6.10, death might result at ~ 1200 m ($\sim 3/4$ mi) at low wind speeds (2 m/sec) from exposure to the expanding puff of chlorine. At high wind speeds, death would be unlikely, according to the calculated pattern of dispersal of the released chlorine.

Low-Level Exposure to Chlorine

A second health-effects question that should be addressed concerning increased use of electric vehicles powered by zinc/chloride batteries is: What are the effects of exposures to low concentrations of chlorine? At what concentrations might low-level exposures become a problem? These questions arise from the perceived possibility that repeated, low-level exposure to chlorine might result from minor accidents that could cause slight leaks in the chlorine flow or storage systems, resulting in a low-level leakage of chlorine during vehicle use or storage.

Minimal detection of chlorine odor has been reported at 0.02 ppm chlorine, with clear perception of odor and identification of chlorine at 0.3 to 0.7 ppm.⁷⁰ Concentrations at which odor is detected varies from individual to individual; older reports have listed 3.5 ppm as the odor threshold concentration.⁶⁴ Perception of odor at low concentrations (< 1 ppm) has also been reported to decrease with time during exposure.⁷⁰ There is an overlap between the range of concentrations that have been found to be minimally detectible (0.02-3.5 ppm) and those that were found to be irritating to the nose and throat (~ 0.09 -1.0 ppm).⁷¹ In one report, exposure of ten individuals at 1 ppm was terminated after 20 min because it was judged to be unbearable.⁷¹ These data indicate a safety factor existing for the zinc/ chloride battery system that does not exist for the lead/acid system, where the potential problem of low-level exposure to stibine is being evaluated. Stibine is a gas that is non-irritating and that has a mild odor even at lethal concentrations. In the case of chlorine, concentrations far below acutely toxic levels cause an avoidance response in humans due to irritation of the nose, throat, eyes, and respiratory tract. An average respiratory irritation threshold concentration of 2.6 ppm (1.95-2.9 ppm range) has been reported for a ten-minute exposure, with an eye irritation threshold of 7.7 ppm.⁷²

The OSHA standard and the threshold limit value (TLV) for chlorine exposure among the occupationally exposed has been set at 1 ppm.⁷³ The values for threshold odor perception indicate that chlorine will be detected by most people at concentrations at or below the TLV. In 1976, NIOSH recommended a short-term exposure limit of 0.5 ppm chlorine for 15 min.⁷⁴ Zielhuis⁶⁵ has recommended the following emergency exposure limits (EEL's) for occupational exposure to chlorine: 60 min, 3 ppm; 30 min, 4 ppm; 15 min, 5 ppm; 5 min, 7 ppm.

Reports on the long-term health of workers occupationally exposed to low levels of chlorine indicate that smokers exposed to chlorine showed decreases in respiratory function not observed in exposed nonsmokers or in nonexposed smokers (decreased DLCO*,⁷⁵ decreased MMF*⁷⁶). A detrimental synergistic

*DLCO = diffusing capacity of lung for carbon monoxide; MMF = maximum mid-expiratory flow rate.

effect between low-level chlorine exposure and smoking therefore appears to exist. In respiratory disease prevalence studies, Patil⁷⁷ and Ferris⁷⁸ found no evidence of permanent lung damage attributable to occupational exposures to low levels of chlorine (0.15 ppm mean concentration for Patil report). Ferris pointed out, however, that a low prevalence of disease in a working population exposed to chlorine may not indicate the 'safety' of low-level chlorine exposure in general populations, where susceptible subgroups may be exposed who are not represented in the work force population.

Recommendations Based on Health Assessment

1. Actual crash test data with analysis of chlorine concentrations in the vicinity of low and high speed crashes are required to give a better estimate of health effects from widespread use of EV's powered by zinc/chloride batteries.

2. If zinc/chloride battery-powered EV's were to become widely used as commuter cars, it might be judicious for cars to carry respirators for occupants to counteract chlorine exposure in the case of an accident. Able-bodied persons within several car lengths of an accident that result in exposure events 1 or 2, Table 6.10, might then be able to get out of the exposure zone before becoming incapacitated. A half-face piece mask with acid-gas canisters might be suitable [In the occupational setting, a chemical cartridge respirator with full face piece, and cartridge(s) and filter(s) providing protection against chlorine is suggested for exposure to chlorine concentrations less than or equal to 25 ppm⁷⁴].

3. Able-bodied occupants in cars trapped in the downwind exposure zone of an accident involving chlorine release should possibly try to move to the upwind area from the site of release.

4. The chlorine pumps of the EV battery possibly should be coupled to a chlorine detector such that the pumps would automatically shut down if chlorine concentrations external to the battery system rose to 5-10 ppm. This would be advantageous in preventing exposure event 2, Table 6.10, where lethal exposures to high chlorine concentrations might otherwise occur.

6.3.2 Titanium

Titanium is an abundant element with many uses in industry and medicine. It is anticipated that titanium will constitute a significant fraction of the Zn/Cl₂ battery module. The purification and fabrication of titanium are associated with potential exposures to titanium tetrachloride (TiCl₄) and titanium particulates (assumed to be TiO₂ or the metal). While industrial experience with TiO₂ indicates that this compound is relatively biologically inert,^{81,82} this is not the case for TiCl₄, a highly corrosive chemical. Acute exposures to liquid TiCl₄ or the vapor are associated with severe burns or chemical bronchitis and/or pneumonia.⁸³

Metabolism

It is estimated from balance studies that approximately 3% of an oral dose of titanium (form or salt of Ti not specified) is absorbed with the major part of the absorbed dose excreted via the urine.⁸⁴ Normal urine concentrations are estimated to be approximately 10 µg/L.⁸⁵ Evidence based on analysis of lung biopsy tissue and autopsy samples suggests that workers occupationally exposed to TiO₂ accumulate significant amounts of TiO₂ in lung alveolar epithelium and neighboring connective tissue.⁸⁶ Lymph node samples from an autopsy case of a TiO₂-exposed worker indicate that lymphatic circulation may be involved in the removal of TiO₂ from the lung.⁸⁶ Exposure of mice to 5 ppm titanium in their drinking water throughout their lives resulted in a significant increase in tissue levels over unexposed control mice. Organs containing significant amounts of titanium included (listed in decreasing order): heart, spleen, lung, kidney, and liver.⁸⁷

No information relative to the absorption or excretion of TiCl₄ was observed in the literature.

Toxicity of Titanium Dioxide

Reports of slight lung fibrosis associated with inhalation exposure to TiO₂ have appeared in the literature.^{88,89} Analysis of tissue samples from three factory workers exposed to TiO₂ pigments for 8-9 years indicated a

slight increase in connective tissue in the pleural, subpleural, and alveolar septal regions of the lung.⁸⁶ Rats exposed via inhalation to TiO_2 (42-328 mppcf) for 9-13 months displayed small focal areas of emphysema in proximity to the larger deposits of dust.⁹⁰ Small blood vessel walls were thickened and hypertrophied. The authors concluded that "there was no evidence of any activity or any specific lesion being produced by titanium dioxide."

Toxicity of Titanium Tetrachloride

Serious burns (chemical and thermal) have resulted from TiCl_4 when workers were splashed with the chemical and then sprayed with water to remove the TiCl_4 .⁸³ Titanium tetrachloride reacts violently with water to produce heat and hydrochloric acid (HCl).⁸³ Permanent eye damage is possible if liquid TiCl_4 is splashed into the eye. Titanium tetrachloride fume is damaging to the lungs, producing chemical bronchitis or pneumonia after acute exposure.⁸³ The corrosive nature of the fume is believed to be responsible for its biological action. A limited study of ten chemical workers exposed for 4-17 years to low levels of TiCl_4 fume (levels not specified) provided no definite evidence of progressive pulmonary dysfunction or pathology.⁸³ Stokinger⁹¹ relates information obtained in a personal communication which states that dogs exposed to TiCl_4 dust (presumed to be a mixture of HCl and TiClO_2) intermittently for a few hours demonstrated respiratory distress. Exposed dogs showed severe bronchitis, edema, collapse and death. Focal congestion and hemorrhage in the lungs of exposed dogs were suggested as characteristic of the effects of HCl on lung tissue. Repeated exposures to TiCl_4 at an average Ti concentration of 8.1 ppm produced tissue reactions similar to those seen after silica exposure.

Summary

Titanium dioxide has been implicated in the etiology of slight fibrotic changes in the lungs of industrially exposed workers. Generally, industrial experience suggests that TiO_2 is relatively innocuous. Titanium tetrachloride is a highly corrosive chemical. Acute exposures to liquid TiCl_4 have produced severe thermal and chemical burns when combined with water. Exposure to TiCl_4 vapors or fume have produced chemical bronchitis or pneumonia in man and animals.

6.3.3 Graphite

It is anticipated that graphite will constitute a significant fraction of Zn/Cl₂ battery systems. Exposures to natural and/or synthetic graphite during processing and fabrication of the carbon electrodes are possible unless appropriate control measures are implemented. Natural and synthetic graphite exposures have been shown to produce pneumoconiosis under heavy exposure conditions.⁹²⁻⁹⁹ The current threshold limit value for graphite (natural) is 15 mppcf (million particles per cubic foot).⁸¹

Clinical Manifestations of Graphite Pneumoconiosis

The ability of graphite to cause pathological changes in the lungs of workers chronically exposed to high concentrations of respirable graphite dust has been recognized for many years. One of the earliest indications that inhalation exposure to graphite was capable of inducing lung injury came from the radiological examination of exposed workers.^{92,93,100} Radiological evidence of graphite pneumoconiosis include pinpoint or macronodular opacities, conglomerate and massive lesions of varying size, and thickening of the pleura.^{96,97} Workers displaying roentgenographic evidence of pneumoconiosis did not always present clinical symptoms of impaired lung function.⁹⁷ The reverse situation has also occurred, i.e., the lack of roentgenographic evidence does not preclude the possibility of pathological changes in the lungs of exposed workers. The more advanced disease state is characterized by dyspnea, cough with sputum production, chest pain, and digital clubbing.^{94,99}

Pathology of Graphite Pneumoconiosis

Postmortem examination of the lungs of workers exposed to graphite have helped to clarify the progression of the disease state.^{96,97,101} The most prevalent pathological findings include: (i) grossly discolored lungs (gray-black to black), (ii) focal and/or diffuse massive fibrosis which can destroy the normal architecture of the lung, (iii) formation of cysts or cavities filled with a black oily fluid (believed to result from an inadequate blood supply to the affected area and culminating in necrosis), (iv) evidence of chronic pneumonitis, and (v) endarteritis (inflammation of the inner arterial wall) and pigmented periarteritis (inflammation of the outer arterial wall).

An unresolved issue in the medical literature on graphite pneumoconiosis is the role of silica (present in natural and synthetic graphite) in the production of lung fibrosis. Recent medical evidence suggests that synthetic graphite or carbon black which contains very little silica can produce pneumoconiosis with progressive massive fibrosis.^{94,95,99} Experimental studies suggest that silica-free graphite can cause diffuse pulmonary fibrosis, but when graphite is combined with small amounts of silica, nodular fibrotic foci develop rapidly.¹⁰² Intratracheal administration of synthetic and natural graphite (containing 0.44 and 12.75% free crystalline silica, respectively) to rats demonstrated a significant difference between the response of the rat lung to the two particulate exposures.⁹⁷ The low-silica graphite produced only a slight response which initially consisted of an "intra-alveolar accumulation of pigmented phagocytes without evidence of any appreciable histocytic proliferation." At a later time point after exposure, the graphite was observed in small scattered foci within the alveolar septa. The graphite containing 12.75% free silica evoked a stronger response-phagocytosis accompanied by progressive cellular inflammation. At 366 days the lungs showed scattered focal lesions pigmented with graphite and were composed of closely packed inflammatory cells.

Summary

Chronic occupational exposure to natural and synthetic graphite has been shown to produce pneumoconiosis in workers exposed many years to high concentrations of respirable-sized dust. Evidence exists that would indicate the disease process can be progressive if exposure has been severe enough. The role of silica in the production of lung fibrosis associated with graphite exposure remains speculative. Experimental results seem to indicate that silica may enhance the fibrogenic potential of graphite.

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7. PERSPECTIVE ON RESULTS

7.1 HUMAN HEALTH AND SAFETY

7.1.1 Major Identifiable Effects

In our evaluation of environmental exposure effects, four agent-specific impacts are presented. Two of the impacts are analyzed in terms of direct mortality risks. They are the carcinogenic potential of vinyl chloride and general excess population mortality resulting from exposure to a combined sulfur oxide and particulate aerosol. In addition, two nonlethal effects are considered. They are an airborne lead impact specified in terms of elevated blood lead levels indicative of adverse response, and a proteinuria effect defined as indicative of kidney damage due to the adverse influence of cadmium exposure. Projected effects of these agents are based on health risk models developed from the published literature.

For each agent, site-specific impacts are analyzed for several likely locations of future battery industry complexes. Pollutant isoconcentration lines are calculated for the pollutant fields surrounding each industry location in a square area 180 km on a side surrounding each site. Individual risk coefficients are calculated for each concentration in the areas between isoconcentration lines. The risk coefficients are then applied to the impacted populations in the respective areas. Sizes of impacted populations are taken from population density values from recent census estimates. Impacts for all isoconcentration areas at a given site are then summed. Analytical results are expressed in terms of numbers of persons potentially responding adversely to exposure to pollutants at industrial sites likely to be used for production of materials required for zinc/halogen battery manufacture.

The incidence of angiosarcoma of the liver as a result of environmental exposure to vinyl chloride monomer in the vicinity of polyvinyl chloride manufacturing sites is estimated to be insignificant (less than $1/10^{11}$).

At Palmerton, Pennsylvania, a site for projected smelting of zinc sulfide ore, environmental exposure to sulfur oxides and particulates, due to production of zinc required for zinc/halogen battery manufacture, is estimated to result in a range of from 5.9 to 31.9 deaths occurring annually in a population of 12,765,000 the range being given by consideration of either the male or female population, and the maximum or minimum exposure conditions (Table 6.1). Reduction in expectation of life, an expression of individual risk, is estimated to range from 0.176 to 0.842 years at the Palmerton, Pennsylvania site. The seemingly large impact of exposure to sulfur oxides and particulates at the Pennsylvania site can therefore be interpreted not so much in an absolute number of deaths, but rather as many small life-shortening events. The impact on the populations at the Corpus Christi, Texas site is estimated to be much smaller, ranging from 0.3 to 0.9 annual deaths, and from 0.196 to 0.387 years of decrease in individual life expectancy, in a population of 994,000.

The number of people estimated to have a blood-lead concentration in excess of 60 µg/dl as a result of zinc production for battery manufacture ranges from 0.26 to 1.07, on an annual basis, in a population of 3.27×10^5 at the Missouri location (Table 6.3). Estimates of responses at the other sites are smaller.

The model for effects of environmental exposure to cadmium provides estimates of excess risk coefficients ranging from 0 to 0.0068 for zinc-producing sites. Pennsylvania is predicted to be the area with the largest excess risk coefficient, and, due to the associated high population density, the number of persons estimated to be at risk annually from renal tubular proteinuria at the end of thirty years, 442 to 701 persons in a population of 12,765,000, appears significant (Table 6.4). Estimates of numbers of persons impacted at the other sites are much smaller and range from 0 to 14 persons annually. It should be remembered that this estimate of risk is an approximation based on a very conservative definition of tubular proteinuria (290 µg β₂-microglobulin per liter of urine).

Health effects among the occupationally exposed are also assessed using the toxicological models in cases where the models can be applied to the occupational setting. The excess risk of developing angiosarcoma of the liver

following a 35-year exposure to 1 ppm vinyl chloride for 8 hr/day, 5 days/week is approximately $2/10^8$. As the size of the occupational work force required for annual production of the polyvinyl chloride required for zinc/chloride battery modules has been estimated at 260 persons (Table 6.9), the number of persons estimated to be at risk of developing angiosarcoma of the liver from occupational exposure to vinyl chloride as a result of zinc/halogen battery manufacture (0.000005 persons) can be considered insignificant. The likelihood of having a blood-lead level defined as hazardous as a result of occupational exposure to lead in a lead industry is estimated at 1 per 100. Since zinc, rather than lead, is the primary product required for zinc/halogen battery production, and since exposure to lead in the occupational setting would result only from the initial presence of lead in the zinc ores, the likelihood of developing an elevated blood-lead level among zinc production workers would be less than 1 per 100. The models for cadmium, and for sulfur oxides and particulates, do not apply to the occupational setting.

With regard to occupational safety, none of the industries required for zinc/halogen battery manufacture are identified as having occupational injury rates substantially higher than those reported for persons employed in other related industries. Most industries have occupational injury rates similar to those for persons employed in the entire private sector. Only persons employed in zinc and titanium primary smelting and refining, and carbon black production, have injury incidence rates higher than those for the entire private sector. From the estimates of workforce sizes for the zinc/chloride battery industries (Table 6.9), it can be seen that the number of annual fatalities estimated from occupational injury is very small (0.1). By comparison, numbers of persons in the environmental setting estimated to be influenced by life-shortening or annual death responses to sulfur oxides and particulates, appear to be much larger.

Estimates of chlorine concentrations produced following accidents involving zinc/chloride battery-powered electric vehicles, indicate that persons in the vicinity of the accidents could be exposed to lethal concentrations of chlorine, with the severity of the exposure depending on the nature of the accident. Actual crash-test data are required to give a better estimate of chlorine concentrations likely to be encountered during accidents involving

electric vehicles powered by zinc/chloride batteries. Chlorine concentrations listed in various sources as being potentially lethal to humans after a 30-minute exposure range from 30 ppm to 430 ppm. The LC50/3 for dogs after a 30-minute exposure is 700-800 ppm. The LC50/4 for three strains of mice after a 30 minute exposure is 100-150 ppm. Whether man is more like dog or like mouse in sensitivity to chlorine appears difficult to establish in the absence of human data on responses to measured chlorine concentrations.

7.1.2 Major Uncertainties

As was previously identified in last year's HEED, four sources of uncertainty remain in any attempt to evaluate toxicological health risk. These sources all relate to the causal relationship itself and its documented scientific support. It is possible to demonstrate causality under experimental conditions. However, in the natural environment, such as that in which epidemiological investigations take place, it is rare that the fortuitous coming together of a well defined and localized population with good exposure data takes place. For the most part the extension of risk models to human health must rely on the strength of association between hypothesized cause and observed outcome, from which causality is inferred.

The uncertainties are divided into four groups: 1) uncertainty in experimental results which tend to support the causal association, 2) the inherent statistical variability of any set of experimental data constrained to small numbers of observations, 3) uptake and metabolism and possible interactions with unobserved agents in the general or individual environment, and 4) the variability of susceptibility among members of populations exposed to similar levels and conditions associated with an industrial-specific agent.

The models presented here represent an informed judgement based on the most current information available. A subjective evaluation of the results would suggest that the model findings are consistent among themselves and are reasonable estimates of likely future level of impacts. They do, however, represent only a small subset of all possible interactions and rely for their validity upon continuous reassessment and addition to the scientific data base.

In the analysis of occupational safety, the grouping of industries together in reporting occupational injury rates limits the certainty with which a given industry can be assigned a given incidence rate. This limitation is dealt with by clearly indicating the SIC code number and industry description used to assign a given rate to a given industry. The uncertainties due to grouping can then be analyzed by the reader. Predictions of occupational safety impacts can also be in error if new industries differ substantially in terms of injury rates from those presently operating. The estimates of workforce size for industries required for zinc/chloride battery production assume a stable efficiency of production, i.e., number of workers employed per MT of product produced. The estimate is admittedly a rough one, but, with its uncertainties, allows the numbers of persons potentially impacted by occupational safety risks to be roughly compared to numbers potentially impacted by risks from occupational health and environmental exposure responses.

Lack of data on responses in humans to measured chlorine concentrations limits our ability to predict effects of EV accidents involving vehicles powered by zinc/chloride batteries. A second uncertainty centers around estimation of anticipated chlorine concentrations in accident situations, pointing up the need for actual crash-test data.

7.1.3 Major Policy Issues

Accidents involving EV's powered by zinc/chloride batteries are estimated to result in generation of potentially lethal concentrations of chlorine under certain accident scenarios. This problem, in addition to the potential for generation of low-level chlorine leaks as a result of low-impact accidents, needs to be further evaluated. Actual crash-test data are required to better estimate chlorine concentrations and sizes of impacted areas around various accident sites.

7.2 ECOLOGICAL IMPACTS

7.2.1 Major Identifiable Effects

We have analyzed atmospheric emission of lead and its deposition at four sites in the country. Subject to the uncertainties which are described

below, we believe that the major identifiable effects on terrestrial and aquatic ecosystems are likely to occur at the Iron County site in Missouri. On an annual basis, if all the atmospheric lead emission from mining and milling is dissolved in rainwater, the lead reaches acute toxic concentrations for several freshwater species up to several kilometers from the site. Gradual build-up of lead in soil could lead to higher concentrations in vegetation and herbivores but our analysis cannot be more specific for long-term deposition without site-specific data.

7.2.2 Major Uncertainties

Dose-response relationships for terrestrial and freshwater organisms which can be extended to ecosystem responses are not available. Lead has complex biogeochemistry which depends on a multitude of physico-chemical and biotic variables. The lead emissions in our analysis have been treated as though they exist as lead and its salts readily available for the uptake and accumulation by biota. Such may not be the case under actual field conditions. The lead emissions and increasing environmental burden of lead is of concern of course, but this lead may not be available to biota for several years. What organisms will be affected is also not quite predictable. If lead remains in solution, the whole trophic chain, including the top carnivore fish, is likely to be affected directly; however, if lead is tied up in the sediments, only the benthic organisms are likely to be affected directly. There is considerable lack of data on how these direct effects translate into indirect effects. For example, there are no data to provide extrapolation of the amount of lead in atmosphere → lead in water → lead in sediments → lead in benthic organisms → lead in trophic chain → lead in top carnivore commercial fish → lead in fish fillet → lead in cooked fish → lead in man. To trace the amount of lead emitted from the battery industry through such a complex chain by means of the current state of knowledge, is virtually impossible. Our approach has relied on some simplistic assumptions and correlations; also we have tried to provide perspective on the extrapolated values by comparing them with lead concentrations found in human milk and with the concentrations permitted in drinking water.

APPENDIX A. FORMULAS FOR CALCULATION OF ATMOSPHERIC DISPERSION AND DEPOSITION

The ground-level atmosphere concentration at a downwind distance x and a cross-wind distance y from a point source, $C(x,y)$, is calculated by the following equation:¹

$$C(x,y) = \frac{Q}{\pi \bar{u}(h) \sigma_y \sigma_z} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] [\text{decay term}] [\text{vertical term}] , \quad (A1)$$

where

$$[\text{decay term}] = \exp [-\lambda x / \bar{u}(h)] , \quad (A2)$$

and

$$\begin{aligned} [\text{vertical term}] = & \sum_n \frac{\phi_n}{2} \left\{ \sum_{i=0}^{\infty} \left[\gamma_n^i \exp \left[-\frac{1}{2} \left(\frac{2iH_m - H + V_{sn}x/\bar{u}(h)}{\sigma_z} \right)^2 \right] \right. \right. \\ & + \gamma_n^{i+1} \exp \left[-\frac{1}{2} \left(\frac{2iH_m + H - (V_{sn}x/\bar{u}(h))}{\sigma_z} \right)^2 \right] \Bigg] \\ & + \sum_{i=1}^{\infty} \left[\gamma_n^i \exp \left[-\frac{1}{2} \left(\frac{2iH_m + H - (V_{sn}x/\bar{u}(h))}{\sigma_z} \right)^2 \right] \right. \\ & \left. \left. + \gamma_n^{i-1} \exp \left[-\frac{1}{2} \left(\frac{2iH_m - H + (V_{sn}x/\bar{u}(h))}{\sigma_z} \right)^2 \right] \right] \right\} . \quad (A3) \end{aligned}$$

In the above Q is the pollutant emission rate, $\bar{u}(h)$ is the mean wind speed at emission height h and σ_y and σ_z are the dispersion coefficients in the cross-wind direction and vertical direction, and λ is the inverse lifetime for the pollutant in the atmosphere. The sum over n is a sum over each particle-size category; ϕ_n , V_{sn} , and γ_n are the mass fraction, gravitational settling velocity, and reflection coefficient for particles in category n . H_m is the mixing height and H is the sum of the emission (stack) height and buoyant plus

momentum rise. σ_z and σ_y are functions of the downwind distance x and the atmospheric stability class and are determined from the Pasquill Gifford curves.² H is calculated using the generalized Briggs plume rise equations.³

The gravitational settling velocity V_{sn} is given by

$$V_{sn} = \frac{\rho_n g d_n^2}{18\mu} \quad , \quad (A4)$$

where ρ_n is the particle density and d_n is the mass median diameter of particles in the n th category. $g = 980 \text{ cm/sec}^2$ (gravity acceleration) and μ is the absolute viscosity of air ($1.83 \times 10^{-4} \text{ g/cm sec}$).⁴ d_n is given by

$$d_n = \left[\frac{d_{1n}^3 + d_{1n}^2 d_{2n} + d_{1n} d_{2n}^2 + d_{2n}^3}{4} \right]^{1/3} \quad , \quad (A5)$$

where d_{1n} and d_{2n} are the respective lower and upper bounds on diameters of particles in the n th category.

For an area source which is a square of side length x_0 , Eq. A1 is replaced by

$$C(x,y) = \frac{Q_A x_0}{\sqrt{2\pi}\bar{u}(h)\sigma_z} \left[\operatorname{erf} \left(\frac{\frac{x_0}{\sqrt{\pi}} + y}{\sqrt{2}\sigma_y} \right) + \operatorname{erf} \left(\frac{\frac{x_0}{\sqrt{\pi}} - y}{\sqrt{2}\sigma_y} \right) \right] \\ \times [\text{vertical term}][\text{decay term}]. \quad (A6)$$

Here, x is the distance to the downwind edge of the square and Q_A is the area source emission rate per unit area. "erf" denotes the error function. The vertical and decay terms are given by Eqs. A2 and A3. For extended area sources which can be divided into different squares $C(x,y)$ is calculated for each square and summed over the squares.

The deposition rate from a point source, $D(x,y)$ is given by:¹

$$D(x,y) = \frac{Q}{2\pi\sigma_y\sigma_z x} \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \exp [-\lambda x / \bar{u}(h)] \times [\text{vert.}], \quad (A7)$$

where

$$\begin{aligned}
 [\text{vert.}] = & \sum_n (1 - \gamma_n) \phi_n \left\{ \left(\bar{b}H + (1 - \bar{b})V_{sn}x/\bar{u}(h) \right) \exp \left[-\frac{1}{2} \left(\frac{H - V_{sn}x/\bar{u}(h)}{\sigma_z} \right)^2 \right] \right. \\
 & + \sum_{i=1}^{\infty} \left[\gamma_n^{i-1} \left(\bar{b}(2iH_m - H) - (1 - \bar{b})V_{sn}x/\bar{u}(h) \right) \exp \left[-\frac{1}{2} \left(\frac{2iH_m - H + V_{sn}x/\bar{u}(h)}{\sigma_z} \right)^2 \right] \right. \\
 & \left. \left. + \gamma_n^i \left(\bar{b}(2iH_m + H) + (1 - \bar{b})V_{sn}x/\bar{u}(h) \right) \exp \left[-\frac{1}{2} \left(\frac{2iH_m + H - V_{sn}x/\bar{u}(h)}{\sigma_z} \right)^2 \right] \right] \right\} \quad (A8)
 \end{aligned}$$

Here all parameters have their previous meanings, and \bar{b} is an average value of the coefficient b in the functional form of $\sigma_z = ax^b$ which is used in Eqs. A1, A3, and A6-A8.

For an area source, $D(x,y)$ is replaced by

$$\begin{aligned}
 D(x,y) = & \frac{Q_A x_0}{\sqrt{2\pi} \sigma_z x} \left[\operatorname{erf} \left(\frac{\frac{x_0}{\sqrt{\pi}} + y}{\sqrt{2} \sigma_y} \right) + \operatorname{erf} \left(\frac{\frac{x_0}{\sqrt{\pi}} - y}{\sqrt{2} \sigma_y} \right) \right] \exp [-\lambda x/\bar{u}(h)] \quad (A9) \\
 & \times [\text{vert.}],
 \end{aligned}$$

where the parameters are as defined before.

Average concentrations or deposition rates are determined by calculating, for a fixed receptor position, values of the atmospheric concentration or deposition rate for successive hours using sequential hourly meteorological data, and averaging over an appropriate period of time (daily, weekly, monthly, seasonal, or annual). Further details are given in Bowers et al.¹

References, Appendix

1. J.F. Bowers, J.R. Bjorklund and C.S. Cheney, "Industrial Source Complex (ISC) Dispersion Model User's Guide" Vols. I and II, H.E. Cramer Co. Inc., Prepared for U.S. Environmental Protection Agency, Reports Nos. EPA-450/ 4-79-030 and EPA-450/4-79-031, December 1979.
2. D.B. Turner, "Workbook of Atmospheric Dispersion Estimates". U.S. Environmental Protection Agency, Revised 1970.
3. G.A. Briggs, "Some Recent Analysis of Plume Rise Observations" in Proceedings of Second International Clean Air Congress, Academic Press New York, 1971.
4. G.A. Briggs, "Diffusion Estimates for Small Emissions" ATDL Contribution File No. 79 (Draft), Air Resources Atmospheric Turbulence and Diffusion Laboratories, Oak Ridge, Tenn. 1973.

APPENDIX B. CHLORINE EXPOSURE CONCENTRATIONS DURING ACCIDENT-RELEASE SCENARIOS

Hydrate Spills

The case most extensively evaluated in the report of Zalosh et al.¹ was that of accidents involving rupture of the chlorine hydrate storage compartment of the zinc/chloride battery, and subsequent release of chlorine following spillage of the stored chlorine hydrate. The scenario was evaluated both by conducting actual chlorine hydrate spill tests and by calculating chlorine concentrations around a spill site based on an appropriate area-source model. During the actual spill tests, chlorine analyzers were placed in various positions downwind from the spill sites at a height of six feet from the ground. Wind speeds were recorded and ranged from 1 to 4 meters per second. Spill test data indicated that following a spill of chlorine hydrate containing 10-20 kg of chlorine (the amount present in an EV battery at 25-50% charge) onto a surface at 32-34°C, rapid evolution of chlorine took place during the first 10 to 20 minutes after the spill, as measured both by chlorine analyzers and by simultaneous measurements of decreases in hydrate mass. Chlorine was evolved such that about four to five spikes of high chlorine concentration were detected per minute during the first 20 minutes. Spikes occurred less often (~2 per minute) during the period from 20 to 50 minutes after the spill. During the first 10 to 20 minutes, while rapid decomposition of the hydrate was still taking place, average chlorine concentrations were at least 30 to 50 ppm at distances 7.6 to 23 meters from the spill (~2 to 7 car lengths away); peak concentrations for the spikes were greater than the analyzers' upper limit, 100 ppm. Concentrations at distances greater than 23 meters were not measured, but, during one test, at 30 meters, people in trailers had to evacuate because of the odor, and chlorine odor was detected at 65 and 500 meters. During the period between 20 and 50 minutes after the spill, when hydrate decomposition was less rapid, average chlorine concentrations at 7.6 meters (~2 car lengths away) were 3-15 ppm, with peak concentrations for

the spikes ranging from 10-80 ppm; at 15 meters average concentrations were 5 ppm, with peak concentrations for the spikes of 12-20 ppm; at 23 meters, average concentrations were 0-7 ppm, with peak concentrations for the spikes of 2-80 ppm. Concentrations closer than 7.6 meters and farther than 23 meters were not measured.

Conclusions from this study are as follows: (1) For a large hydrate spill, in which most of the chlorine hydrate stored in a partially charged EV battery comes in contact with warm pavement, a danger zone exists, during the first 10 to 20 minutes after the spill, where chlorine concentrations average at least 30 to 50 ppm with frequent intermittent spikes exceeding 100 ppm. The danger zone is a sector downwind from the spill site with an angle of about 30° and a radius of at least 23 meters (~7 car lengths; greater distances not studied). At times between 20 and 50 minutes after the spill, average concentrations in the zone studied ranged from 3-15 ppm at 7.6 meters downwind from the spill to 0-7 ppm at 23 meters. (2) The concentrations mentioned above might be low for several reasons: (a) If a 50-kWh electric vehicle battery were fully charged at the time of an accident, the chlorine hydrate in the battery would contain an equivalent of 40 kg of chlorine, or two to four times as much as was used in the hydrate spill tests. (b) Actual average concentrations during the first 20 minutes after the spill tests were probably greater than 30 to 50 ppm, since a significant number of off-scale readings were used by the instrument to derive the average. (c) The chlorine analyzers were six feet above the ground, and higher concentrations of the dense chlorine gas might be experienced by children or injured persons lying on the ground; and (d) Concentrations directly at the site of the spill were not measured. Closest measurements were taken at 7.6 meters, about two car lengths from the spill. Those trapped in the car involved in the accident would be closer and concentrations might be higher (or lower) for them.

Electrical vehicle accident scenarios other than the chlorine hydrate spill, and involving a release of chlorine, were analyzed in the reference hazard assessment report.¹ For these additional scenarios, anticipated chlorine exposure concentrations were estimated through calculations; models for dispersion of chlorine were used under various conditions for chlorine release. Exposure estimates for these additional accident scenarios are presented in Table 6.10 of the main report, along with those from the hydrate spill test.

Rupture of Chlorine Flow Lines

During discharge of the zinc/chloride electric vehicle battery, chlorine is flowing at a rate of 40 liters/minute in the lines between the chlorine hydrate store and the battery stack. During charge, the chlorine flow rate is 28 liters per minute. If, during an accident, line ruptures occur without shutting down the chlorine pumping system, chlorine would be released continuously at the given pumping rate. The calculations of Zalosh et al.¹ predict that for a stable atmosphere (2 meters/second wind speed), continuous release of chlorine at 40 L/min would produce a two-meter-wide area extending to 30 meters downwind from the accident site (10 car lengths) and rising to 0.3 meters (~1 ft) in height, that would contain chlorine at a concentration greater than 100 ppm. This danger area with chlorine concentrations greater than 100 ppm would extend to only six meters downwind under unstable wind conditions (5 m/sec). Areas containing irritating concentrations of chlorine would be much larger. Unlike the case of hydrate spill, where the major part of the release would occur over a short period of time, this scenario has the potential to produce steady-state levels that could be maintained for a longer period of time. (At a release rate of 40 L/min only 10% of the chlorine in a fully-charged 50-kWh battery would be released in about 30 minutes.)

Instantaneous Chlorine Release

Calculations were made for chlorine dispersion following two accident-related, instantaneous release scenarios.¹ The first involved rupture of the cell stack compartment with instantaneous release of the 28 liters (1 ft³) of chlorine present in the vapor space in the battery cell stack. Using an "expanding puff" dispersion model, it was estimated that during this 28-liter release, a bystander might be exposed to a chlorine concentration greater than 100 ppm for about six seconds at a wind speed of 2 m/sec or for less time at higher wind speeds. The second scenario analyzed for instantaneous chlorine release was the most drastic one possible. It involved instantaneous release of the entire chlorine content of the battery (41 kg chlorine, or 12.8 m³), as from some type of internal or external explosion. Following this scenario, it was estimated that during unstable wind conditions, the maximum time of exposure to chlorine concentrations greater than 50 ppm would be 17 seconds, and would

occur at 300 meters downwind from the release sight. Under stable wind conditions (2 m/sec), the longest exposure to chlorine concentrations greater than 50 ppm was estimated to be 70 seconds and would occur at 1200 meters (1/5 to 1/4 mile) downwind from the site of release.

Chlorine Release Inside a Tunnel

Average chlorine concentrations inside a tunnel due to a chlorine hydrate spill or a chlorine line rupture were calculated using a simple equation for mixing of gases inside a longitudinally ventilated tunnel. For a large hydrate spill, calculated average chlorine concentrations ranged from 9.5 to 19 ppm, depending on tunnel ventilation rate. For a small hydrate spill, calculated average chlorine concentrations ranged from 0.6 to 1.2 ppm. Following rupture of chlorine flow lines during discharge (40 L/min chlorine release rate), calculated average chlorine concentrations ranged from 2.4 to 4.9 ppm. These average concentrations for the whole tunnel, however, were estimated to apply only to areas of the tunnel beyond 200 m (~70 car lengths) from the accident site. Within a distance of 200 m from the release site, local concentrations were not calculated, but would be significantly higher than the calculated average concentrations.

Continuous Low-Level Chlorine Release

Accidents could occur that might cause slight leaks in the chlorine flow or storage systems. Continuous low-level exposure to chlorine might thus occur during vehicle use or storage, and potential health effects from low-level chlorine exposure as well as acute exposure should be evaluated.

References, Appendix B

R.G. Zalosh et al., "Hazard Assessment of Zinc-Chlorine Electric Vehicle Batteries", Factor Mutual Research Corporation, Norwood, MA, Report No. OC1N8.RK (1979). C00-5088-1.

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